

Document made available under the Patent Cooperation Treaty (PCT)

International application number: PCT/US05/008917

International filing date: 17 March 2005 (17.03.2005)

Document type: Certified copy of priority document

Document details: Country/Office: US
Number: 60/553,906
Filing date: 17 March 2004 (17.03.2004)

Date of receipt at the International Bureau: 20 April 2005 (20.04.2005)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b)



World Intellectual Property Organization (WIPO) - Geneva, Switzerland
Organisation Mondiale de la Propriété Intellectuelle (OMPI) - Genève, Suisse

1307664

THE UNITED STATES OF AMERICA

TO ALL TO WHOM THESE PRESENTS SHALL COME:

UNITED STATES DEPARTMENT OF COMMERCE

United States Patent and Trademark Office

April 12, 2005

THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A FILING DATE.

APPLICATION NUMBER: 60/553,906

FILING DATE: *March 17, 2004*

RELATED PCT APPLICATION NUMBER: *PCT/US05/08917*



Certified by

Under Secretary of Commerce
for Intellectual Property
and Director of the United States
Patent and Trademark Office

PROVISIONAL APPLICATION COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION under 35 CFR 1.53 (c).

Docket Number		63558		Type a plus sign (+) inside this box	+
INVENTOR(S)/APPLICANT(S)					
LAST NAME	FIRST NAME	MIDDLE INITIAL	RESIDENCE (CITY AND EITHER STATE OR FOREIGN COUNTRY)		
Arriola	Daniel	J.	2100 E. Mier Road, Midland, MI 48642		
Bokota	Marilyn		4431 West Lang, Beaverton, MI 48612		
Carnahan	Edmund	M.	4619 Twin Elm Drive, Fresno, TX 77545		
Devore	David	D.	4901 E. Shaffer Road, Midland, MI 48642		
Hustad	Phillip	D.	3618 Rose Water Court, Manvel, TX 77578		
<input checked="" type="checkbox"/> Additional inventors are being named on separately numbered sheets attached hereto					
TITLE OF THE INVENTION (280 characters max)					
CATALYST COMPOSITION COMPRISING SHUTTLLING AGENT FOR ETHYLENE COPOLYMER FORMATION					
CORRESPONDENCE ADDRESS					
THE DOW CHEMICAL COMPANY Intellectual Property P. O. Box 1967 Midland, MI 48641-1967 U.S.A.			Telephone: 989-636-2540 Fax: 989-636-3237		
ENCLOSED APPLICATION PARTS (check all that apply)					
<input checked="" type="checkbox"/> Specification		Number of Pages <u>44</u>		<input type="checkbox"/> Small Entity Statement	
<input type="checkbox"/> Drawing(s)		Number of Sheets _____		<input type="checkbox"/> Other (specify) _____	
METHOD OF PAYMENT (check one)					
<input type="checkbox"/> A check or money order is enclosed to cover the Provisional filing fees			PROVISIONAL FILING FEE AMOUNT		\$160.00
<input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge filing fees and credit Deposit Account Number: <u>No. 04-1512</u>					
The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government					
<input checked="" type="checkbox"/> No					
<input type="checkbox"/> Yes, the name of the U.S. Government agency and the Government contract number are: _____					

Respectfully submitted,



Douglas N. Deline

Registration No.: 29,146

Phone No.: (989) 636 - 2938

EXPRESS MAIL MAILING NO.: EV 331 476 521 US
DATE OF DEPOSIT: March 17, 2004

CSS

PROVISIONAL APPLICATION FILING ONLY

PROVISIONAL APPLICATION COVER SHEET

Page 2

			Docket Number	63558
TITLE OF THE INVENTION (280 characters max)				
CATALYST COMPOSITION COMPRISING SHUTTLLING AGENT FOR ETHYLENE COPOLYMER FORMATION				
INVENTOR(s)/APPLICANT(s) - Continued				
LAST NAME	FIRST NAME	MIDDLE INITIAL	RESIDENCE (CITY AND EITHER STATE OR FOREIGN COUNTRY)	
Kuhlman	Roger	L.	2533 Spring Street, Charleston, WV 25303	
Stirn	Pamela	J.	1120 W. Stewart Road, Midland, MI 48640	
Wenzel	Timothy	T.	888 Poplar Road, Charleston, WV 25302	

PROVISIONAL APPLICATION FILING ONLY

CATALYST COMPOSITION COMPRISING SHUTTLING AGENT FOR ETHYLENE COPOLYMER FORMATION

Background of the Invention

5 The present invention relates to catalyst compositions for polymerization of mixtures of ethylene and one or more comonomers and to a process for preparing copolymers therefrom. The resulting copolymers comprise two or more differing regions or segments causing the copolymer to possess unique physical properties. These copolymers and polymeric blends comprising the same are usefully employed in the preparation of solid articles such as moldings, films, and sheets, 10 foamed objects by molding, extruding, or other processes, and are useful as components or ingredients in adhesives, laminates, polymeric blends, and other end uses. The resulting products are used in the manufacture of components for automobiles, such as profiles, bumpers and trim parts; packaging materials; electric cable insulation, and other applications.

 The use of certain metal alkyl compounds and other compounds, such as hydrogen, as chain 15 transfer agents to interrupt chain growth in olefin polymerizations is well known in the art. In addition, it is known to employ such compounds, especially aluminum alkyl compounds, as scavengers or as cocatalysts in olefin polymerizations. In Macromolecules, 33, 9192-9199 (2000) the use of certain aluminum trialkyl compounds as chain transfer agents in combination with certain paired zirconocene catalyst compositions resulted in polypropylene mixtures containing small 20 quantities of polymer fractions containing both isotactic and atactic chain segments. In Liu and Rytter, Macromolecular Rapid Comm., 22, 952-956 (2001) and Bruaseth and Rytter, Macromolecules, 36, 3026-3034 (2003) mixtures of ethylene and 1-hexene was polymerized by a similar catalyst composition containing trimethylaluminum chain transfer agent. In the latter reference, the authors summarized the prior art studies in the following manner (some citations 25 omitted):

 Mixing of two metallocenes with known polymerization behavior can be used to control polymer microstructure. Several studies have been performed of ethene polymerization by mixing two metallocenes. Common observations were that, by combining catalysts which separately give polyethene with different *M_w*, polyethene with broader and in some cases bimodal MWD can be 30 obtained. [S]oares and Kim (J. Polym. Sci., Part A: Polym. Chem., 38, 1408-1432 (2000)) developed a criterion in order to test the MWD bimodality of polymers made by dual single-site catalysts, as exemplified by ethene/1-hexene copolymerization of the mixtures Et(Ind)₂ZrCl₂/Cp₂HfCl₂ and Et(Ind)₂ZrCl₂/ CGC (constrained geometry catalyst) supported on silica. Heiland and Kaminsky (Makromol. Chem., 193, 601-610 (1992)) studied a mixture of Et- 35 (Ind)₂ZrCl₂ and the hafnium analogue in copolymerization of ethene and 1-butene.

These studies do not contain any indication of interaction between the two different sites, e.g., by readsorption of a terminated chain at the alternative site. Such reports have been issued, however, for polymerization of propene. Chien et al. (J. Polym. Sci., Part A: Polym. Chem., 37, 2439-2445 (1999), Makromol., 30, 3447-3458 (1997)) studied propene polymerization by homogeneous binary zirconocene catalysts. A blend of isotactic polypropylene (i-PP), atactic polypropylene (a-PP), and a stereoblock fraction (i-PP-*b*-a-PP) was obtained with a binary system comprising an isospecific and an aspecific precursor with a borate and TIBA as cocatalyst. By using a binary mixture of isospecific and syndiospecific zirconocenes, a blend of isotactic polypropylene (i-PP), syndiotactic polypropylene (s-PP), and a stereoblock fraction (i-PP-*b*-s-PP) was obtained. The mechanism for formation of the stereoblock fraction was proposed to involve the exchange of propagating chains between the two different catalytic sites. Przybyla and Fink (Acta Polym., 50, 77-83 (1999)) used two different types of metallocenes (isospecific and syndiospecific) supported on the same silica for propene polymerization. They reported that, with a certain type of silica support, chain transfer between the active species in the catalyst system occurred, and stereoblock PP was obtained. Lieber and Brintzinger (Macromol. 3, 9192-9199 (2000)) have proposed a more detailed explanation of how the transfer of a growing polymer chain from one type of metallocene to another occurs. They studied propene polymerization by catalyst mixtures of two different *ansa*-zirconocenes. The different catalysts were first studied individually with regard to their tendency toward alkyl-polymeryl exchange with the alkylaluminum activator and then pairwise with respect to their capability to produce polymers with a stereoblock structure. They reported that formation of stereoblock polymers by a mixture of zirconocene catalysts with different stereoselectivities is contingent upon an efficient polymeryl exchange between the Zr catalyst centers and the Al centers of the cocatalyst."

Brusath and Rytter then disclosed their own observations using paired zirconocene catalysts to polymerize mixtures of ethylene/1-hexene and reported the effects of the influence of the dual site catalyst on polymerization activity, incorporation of comonomer, and polymer microstructure using methylalumoxane cocatalyst.

Analysis of the foregoing results indicate that Rytter and coworkers likely failed to utilize combinations of catalyst, cocatalyst, and third components that were capable of reabsorption of the polymer chain from the chain transfer agent onto both of the active catalytic sites, i.e., two-way reabsorption. While indicating that chain termination due to the presence of trimethylaluminum likely occurred with respect to polymer formed from the catalyst incorporating minimal comonomer, and thereafter that polymeryl exchange with the more open catalytic site followed by continued polymerization likely occurred, evidence of the reverse flow of polymer ligands appeared to be lacking in the reference. Accordingly, the polymer product formed by the foregoing prior art

method likely was limited to at most, two segments or blocks of differing density or comonomer incorporation. Moreover, the resulting copolymer products apparently possessed broadened molecular weight distributions of 3.0 or greater. Little evidence of actual block copolymer formation was provided.

Moreover, because the cocatalyst employed by Bruaseth and Rytter (methylalumoxane) contained residual quantities of trimethylaluminum (which was also the chain transfer agent employed in their research), and because a large excess of such cocatalyst was employed (Al:Zr = 3000), the method disclosed by these researchers provided no independent ability to vary the quantity or type of chain transfer agent. Similar results are reported in WO98/34970, where dual metallocene catalysts and MAO cocatalysts were employed to prepare thermoplastic elastomers of relatively broad molecular weight distribution.

It would be desirable if there were provided an improved process for preparing multiblock copolymers of ethylene and a comonomer by the use of a shuttling agent. In addition it would be desirable to provide such an improved process that is capable of preparing copolymers having a relatively narrow molecular weight distribution. It would further be desirable to provide an improved process for preparing copolymers having more than two segments or blocks. Finally, it would be desirable to provide an improved process for preparing any of the foregoing desirable polymer products that allows for independent control of the quantity and identity of the shuttling agent employed.

Summary of the Invention

According to the present invention there are now provided a catalyst composition for use in polymerization of ethylene and at least one copolymerizable comonomer, to form a high molecular weight, segmented, ethylene copolymer, said copolymer containing therein two or more, preferably three or more segments differing in comonomer content or density, the catalyst composition comprising the admixture or reaction product resulting from combining:

(A) a first metal complex olefin polymerization catalyst having a high comonomer incorporation index,

(B) a second metal complex olefin polymerization catalyst having a comonomer incorporation index less than 95 percent, preferably less than 90 percent, more preferably less than 25 percent, and most preferably less than 10 percent of the comonomer incorporation index of catalyst (A), and

(C) a chain shuttling agent.

In a further embodiment of the present invention there is provided a process for preparing a high molecular weight, segmented, copolymer of ethylene and one or more addition polymerizable monomers other than ethylene, said process comprising contacting one or more addition

polymerizable monomers under addition polymerization conditions with a catalyst composition comprising:

the admixture or reaction product resulting from combining:

- 5 (A) a first metal complex olefin polymerization catalyst having a high comonomer incorporation index,
- (B) a second metal complex olefin polymerization catalyst having a comonomer incorporation index less than 90 percent, preferably less than 50 percent, most preferably less than 5 percent of the comonomer incorporation index of catalyst (A), and
- (C) a chain shuttling agent.

10 In another embodiment of the invention there is provided a high molecular weight, segmented, ethylene copolymer, said copolymer containing therein two or more, preferably three or more segments differing in comonomer content or density. Highly preferably the copolymer possesses a molecular weight distribution, Mw/Mn, of less than 3.0, preferably less than 2.8.

15 In a still further embodiment of the present invention, there is provided a polymer mixture comprising: (1) a homopolymer of ethylene and/or a copolymer of ethylene and a copolymerizable comonomer and (2) a high molecular weight, segmented, copolymer of ethylene and one or more addition polymerizable monomers other than ethylene according to the present invention or prepared according to the process of the present invention.

Detailed Description of the Invention

20 All references to the Periodic Table of the Elements herein shall refer to the Periodic Table of the Elements, published and copyrighted by CRC Press, Inc., 2003. Also, any references to a Group or Groups shall be to the Groups or Groups reflected in this Periodic Table of the Elements using the IUPAC system for numbering groups. For purposes of United States patent practice, the contents of any patent, patent application, or publication referenced herein are hereby incorporated

25 by reference in their entirety (or the equivalent US version thereof is so incorporated by reference) especially with respect to the disclosure of synthetic techniques and general knowledge in the art.

The term “comprising” and derivatives thereof is not intended to exclude the presence of any additional component, step or procedure, whether or not the same is disclosed herein. In order to avoid any doubt, all compositions claimed herein through use of the term “comprising” may

30 include any additional additive, adjuvant, or compound whether polymeric or otherwise, unless stated to the contrary. In contrast, the term, “consisting essentially of” excludes from the scope of any succeeding recitation any other component, step or procedure, excepting those that are not essential to operability. The term “consisting of” excludes any component, step or procedure not specifically delineated or listed. The term “or”, unless stated otherwise, refers to the listed

35 members individually as well as in any combination.

The term “polymer”, includes both homopolymers, that is, homogeneous polymers prepared from a single reactive compound, and copolymers, meaning polymers prepared by reaction of at least two polymer forming, reactive compounds. More specifically, the term “polyethylene” includes homopolymers of ethylene and copolymers of ethylene and one or more C₃₋₈ α -olefins.

- 5 The term “crystalline” if employed, refers to a polymer that exhibits an X-ray diffraction pattern at 25 °C and possesses a first order transition or crystalline melting point (T_m). The term may be used interchangeably with the term “semicrystalline”.

- The term, “shuttling agent” refers to a compound or mixture of compounds employed in the catalyst composition of the present invention that is capable of causing polymeryl exchange
- 10 between at least two active catalyst sites of the catalyst composition under the conditions of the polymerization. That is, exchange occurs both to and from at least two active catalyst sites. Preferably the shuttling agent has an activity ratio R_{A-B}/R_{B-A} of from 0.1 and 100, more preferably from 0.3 to 10, most preferably from 0.5 to 5, and most highly preferably from 0.8 to 2, wherein R_{A-B} is the rate of polymeryl exchange from catalyst A active site to catalyst B active site via the
- 15 shuttling agent, and R_{B-A} is the rate of reverse polymeryl exchange, i.e., the rate of exchange from catalyst B active site to catalyst A active site via the shuttling agent. Desirably, the intermediate formed between the shuttling agent and the polymeryl chain is sufficiently stable that chain termination is relatively rare. Desirably, less than 10 percent, preferably less than 50 percent, more preferably less than 75 percent and most desirably less than 90 percent of shuttle-polymeryl
- 20 products are terminated prior to attaining 3 distinguishable polymer segments or blocks.

- By selecting different combinations of catalysts having differing comonomer incorporation rates as well as differing reactivities, and by pairing different shuttling agents or mixtures of agents with these catalyst combinations, polymer products having segments of different densities or comonomer concentrations, different block lengths, and different numbers of such segments or
- 25 blocks in each copolymer can be prepared. For example, if the activity of the shuttling agent is low relative to the catalyst polymer chain propagation rate, a polymer blend is obtained. Contrariwise, if shuttling is very fast relative to polymer chain propagation, a copolymer having a random chain structure is obtained. By proper selection of both catalyst mixture and shuttling agent, relatively pure block copolymers, copolymers containing relatively large polymer segments or blocks, and/or
- 30 blends of the foregoing with various ethylene homopolymers and/or copolymers can be obtained.

Suitable shuttling agents for use herein include Group 12 or 13 metal compounds or complexes containing at least one C₁₋₂₀ hydrocarbyl group, preferably trihydrocarbyl aluminum compounds or dihydrocarbyl zinc compounds containing from 1 to 12 carbons in each hydrocarbyl group. Preferred hydrocarbyl groups are alkyl groups, preferably linear or branched, C₂₋₄ alkyl

groups. Most preferred shuttling agents for use in the present invention are triethyl aluminum and diethyl zinc.

The term, "comonomer incorporation index", refers to the percent comonomer incorporated into a copolymer prepared under representative ethylene/ comonomer polymerization conditions by the catalyst under consideration in the absence of other polymerization catalysts, ideally under steady-state, continuous solution polymerization conditions in a hydrocarbon at 100 °C, 4.5 MPa ethylene pressure, greater than 95 percent ethylene conversion, and greater than 0.01 percent comonomer conversion. The selection of metal complexes or catalyst compositions having the greatest difference in comonomer incorporation indices results in copolymers having the largest difference in block or segment properties, such as density.

Metal complexes for use herein having high comonomer incorporation index (Catalyst A) include complexes of transition metals selected from Groups 4-8 of the Periodic Table of the Elements, preferably Group 4, i.e., titanium, zirconium and hafnium, containing one or more delocalized, π -bonded ligands or polyvalent Lewis base ligands. Examples include metallocene, half-metallocene, constrained geometry, and polyvalent pyridylamine base complexes. The complexes are generically depicted by the formula: $MK_kX_xZ_z$, or a dimer thereof, wherein

M is a transition metal selected from Groups 3-10 of the Periodic Table of the Elements, preferably of a metal of Groups 4-8, most preferably a Group 4 metal;

K independently each occurrence is a group containing delocalized π -electrons through which K is bound to M, said K group containing up to 50 atoms not counting hydrogen atoms, optionally two or more K groups may be joined together forming a bridged structure, and further optionally one or more K groups may be bound to Z, to X or to both Z and X;

X independently each occurrence is a monovalent, anionic moiety having up to 40 non-hydrogen atoms, optionally one or more X groups may be bonded together thereby forming a divalent or polyvalent anionic group, and, further optionally, one or more X groups and one or more Z groups may be bonded together thereby forming a moiety that is both covalently bound to M and coordinated thereto;

Z independently each occurrence is a neutral, Lewis base donor ligand of up to 50 non-hydrogen atoms containing at least one unshared electron pair through which Z is coordinated to M;

k is an integer from 0 to 3;

x is an integer from 1 to 4;

z is a number from 0 to 3; and

the sum, $k+x$, is equal to the formal oxidation state of M.

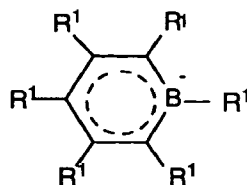
Suitable metal complexes include those containing from 1 to 3 π -bonded anionic or neutral ligand groups, which may be cyclic or non-cyclic delocalized π -bonded anionic ligand groups.

Exemplary of such π -bonded groups are conjugated or nonconjugated, cyclic or non-cyclic diene and dienyl groups, allyl groups, boratabenzene groups, phosphole, and arene groups. By the term " π -bonded" is meant that the ligand group is bonded to the transition metal by a sharing of electrons from a partially delocalized π -bond.

5 Each atom in the delocalized π -bonded group may independently be substituted with a radical selected from the group consisting of hydrogen, halogen, hydrocarbyl, halohydrocarbyl, hydrocarbyl-substituted heteroatoms wherein the heteroatom is selected from Group 14-16 of the Periodic Table of the Elements, and such hydrocarbyl- substituted heteroatom radicals further substituted with a Group 15 or 16 hetero atom containing moiety. In addition two or more such
10 radicals may together form a fused ring system, including partially or fully hydrogenated fused ring systems, or they may form a metallocycle with the metal. Included within the term "hydrocarbyl" are C_{1-20} straight, branched and cyclic alkyl radicals, C_{6-20} aromatic radicals, C_{7-20} alkyl-substituted aromatic radicals, and C_{7-20} aryl-substituted alkyl radicals. Suitable hydrocarbyl-substituted heteroatom radicals include mono-, di- and tri-substituted radicals of boron, silicon, germanium,
15 nitrogen, phosphorus or oxygen wherein each of the hydrocarbyl groups contains from 1 to 20 carbon atoms. Examples include N,N-dimethylamino, pyrrolidinyl, trimethylsilyl, triethylsilyl, t-butyl dimethylsilyl, methyl di(t-butyl)silyl, triphenylgermyl, and trimethylgermyl groups. Examples of Group 15 or 16 hetero atom containing moieties include amino, phosphino, alkoxy, or alkylthio moieties or divalent derivatives thereof, e. g. amide, phosphide, alkyleneoxy or alkylene thio groups
20 bonded to the transition metal or Lanthanide metal, and bonded to the hydrocarbyl group, π -bonded group, or hydrocarbyl- substituted heteroatom.

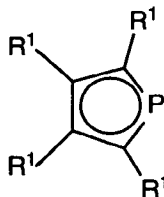
Examples of suitable anionic, delocalized π -bonded groups include cyclopentadienyl, indenyl, fluorenyl, tetrahydroindenyl, tetrahydrofluorenyl, octahydrofluorenyl, pentadienyl, cyclohexadienyl, dihydroanthracenyl, hexahydroanthracenyl, decahydroanthracenyl groups,
25 phosphole, and boratabenzyl groups, as well as inertly substituted derivatives thereof, especially C_{1-10} hydrocarbyl- substituted or tris(C_{1-10} hydrocarbyl)silyl- substituted derivatives thereof. Preferred anionic delocalized π -bonded groups are cyclopentadienyl, pentamethylcyclopentadienyl, tetramethylcyclopentadienyl, tetramethylsilylcyclopentadienyl, indenyl, 2,3-dimethylindenyl, fluorenyl, 2-methylindenyl, 2-methyl-4-phenylindenyl, tetrahydrofluorenyl, octahydrofluorenyl, 1-
30 indacenyl, 3-pyrrolidinoinden-1-yl, 3,4-(cyclopenta(*l*))phenanthren-1-yl, and tetrahydroindenyl.

The boratabenzyl ligands are anionic ligands which are boron containing analogues to benzene. They are previously known in the art having been described by G. Herberich, et al., in Organometallics, 14,1, 471-480 (1995). Preferred boratabenzenes correspond to the formula:



wherein R^1 is an inert substituent, preferably selected from the group consisting of hydrogen, hydrocarbyl, silyl, halo or germyl, said R^1 having up to 20 atoms not counting hydrogen, and optionally two adjacent R^1 groups may be joined together. In complexes involving divalent derivatives of such delocalized π -bonded groups one atom thereof is bonded by means of a covalent bond or a covalently bonded divalent group to another atom of the complex thereby forming a bridged system.

Phospholes are anionic ligands that are phosphorus containing analogues to a cyclopentadienyl group. They are previously known in the art having been described by WO 98/50392, and elsewhere. Preferred phosphole ligands correspond to the formula:



wherein R^1 is as previously defined.

Preferred transition metal complexes for use herein correspond to the formula: $MK_kX_xZ_z$, or a dimer thereof, wherein:

M is a Group 4 metal;

K is a group containing delocalized π -electrons through which K is bound to M, said K group containing up to 50 atoms not counting hydrogen atoms, optionally two K groups may be joined together forming a bridged structure, and further optionally one K may be bound to X or Z;

X each occurrence is a monovalent, anionic moiety having up to 40 non-hydrogen atoms, optionally one or more X and one or more K groups are bonded together to form a metallocycle, and further optionally one or more X and one or more Z groups are bonded together thereby forming a moiety that is both covalently bound to M and coordinated thereto;

Z independently each occurrence is a neutral, Lewis base donor ligand of up to 50 non-hydrogen atoms containing at least one unshared electron pair through which Z is coordinated to M;

k is an integer from 0 to 3;

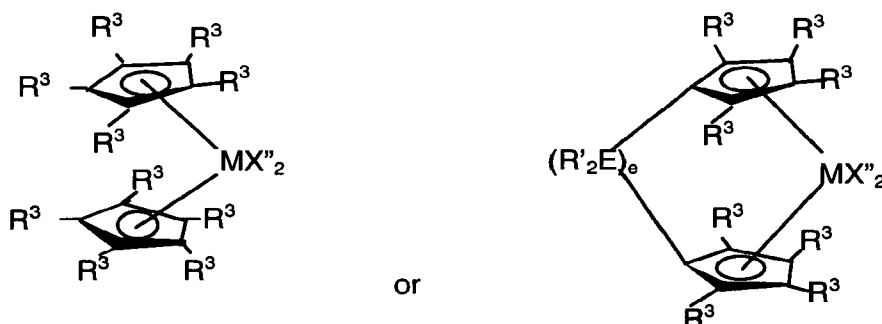
x is an integer from 1 to 4;

z is a number from 0 to 3; and

the sum, $k+x$, is equal to the formal oxidation state of M.

Preferred complexes include those containing either one or two K groups. The latter complexes include those containing a bridging group linking the two K groups. Preferred bridging groups are those corresponding to the formula $(ER'_2)_e$ wherein E is silicon, germanium, tin, or carbon, R' independently each occurrence is hydrogen or a group selected from silyl, hydrocarbyl, hydrocarbyloxy and combinations thereof, said R' having up to 30 carbon or silicon atoms, and e is 1 to 8. Preferably, R' independently each occurrence is methyl, ethyl, propyl, benzyl, tert-butyl, phenyl, methoxy, ethoxy or phenoxy.

Examples of the complexes containing two K groups are compounds corresponding to the formula:



wherein:

M is titanium, zirconium or hafnium, preferably zirconium or hafnium, in the +2 or +4 formal oxidation state;

R³ in each occurrence independently is selected from the group consisting of hydrogen, hydrocarbyl, silyl, germyl, cyano, halo and combinations thereof, said R³ having up to 20 non-hydrogen atoms, or adjacent R³ groups together form a divalent derivative (that is, a hydrocarbadiyl, siladiyl or germadiyl group) thereby forming a fused ring system, and

X'' independently each occurrence is an anionic ligand group of up to 40 non-hydrogen atoms, or two X'' groups together form a divalent anionic ligand group of up to 40 non-hydrogen atoms or together are a conjugated diene having from 4 to 30 non-hydrogen atoms bound by means of delocalized π -electrons to M, whereupon M is in the +2 formal oxidation state, and

R', E and e are as previously defined.

Exemplary bridged ligands containing two π -bonded groups are:

dimethylbis(cyclopentadienyl)silane, dimethylbis(tetramethylcyclopentadienyl)silane, dimethylbis(2-ethylcyclopentadien-1-yl)silane, dimethylbis(2-*t*-butylcyclopentadien-1-yl)silane, 2,2-bis(tetramethylcyclopentadienyl)propane, dimethylbis(inden-1-yl)silane, dimethylbis(tetrahydroinden-1-yl)silane, dimethylbis(fluoren-1-yl)silane, dimethylbis(tetrahydrofluoren-1-yl)silane, dimethylbis(2-methyl-4-phenylinden-1-yl)silane, dimethylbis(2-methylinden-1-yl)silane, dimethyl(cyclopentadienyl)(fluoren-1-yl)silane,

dimethyl(cyclopentadienyl)(octahydrofluoren-1-yl)silane,
 dimethyl(cyclopentadienyl)(tetrahydrofluoren-1-yl)silane, (1, 1, 2, 2-tetramethy)-1, 2-
 bis(cyclopentadienyl)disilane, (1, 2-bis(cyclopentadienyl)ethane, and dimethyl(cyclopentadienyl)-1-
 (fluoren-1-yl)methane.

- 5 Preferred X'' groups are selected from hydride, hydrocarbyl, silyl, germyl, halohydrocarbyl, halosilyl, silylhydrocarbyl and aminohydrocarbyl groups, or two X'' groups together form a divalent derivative of a conjugated diene or else together they form a neutral, π -bonded, conjugated diene. Most preferred X'' groups are C₁₋₂₀ hydrocarbyl groups.

Examples of metal complexes of the foregoing formula suitable for use in the present
 10 invention include:

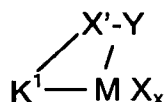
- bis(cyclopentadienyl)zirconiumdimethyl,
 bis(cyclopentadienyl)zirconium dibenzyl,
 bis(cyclopentadienyl)zirconium methyl benzyl,
 bis(cyclopentadienyl)zirconium methyl phenyl,
 15 bis(cyclopentadienyl)zirconiumdiphenyl,
 bis(cyclopentadienyl)titanium-allyl,
 bis(cyclopentadienyl)zirconiummethylmethoxide,
 bis(cyclopentadienyl)zirconiummethylchloride,
 bis(pentamethylcyclopentadienyl)zirconiumdimethyl,
 20 bis(pentamethylcyclopentadienyl)titaniumdimethyl,
 bis(indenyl)zirconiumdimethyl,
 indenylfluorenylzirconiumdimethyl,
 bis(indenyl)zirconiummethyl(2-(dimethylamino)benzyl),
 bis(indenyl)zirconiummethyltrimethylsilyl,
 25 bis(tetrahydroindenyl)zirconiummethyltrimethylsilyl,
 bis(pentamethylcyclopentadienyl)zirconiummethylbenzyl,
 bis(pentamethylcyclopentadienyl)zirconiumdibenzyl,
 bis(pentamethylcyclopentadienyl)zirconiummethylmethoxide,
 bis(pentamethylcyclopentadienyl)zirconiummethylchloride,
 30 bis(methylethylcyclopentadienyl)zirconiumdimethyl,
 bis(butylcyclopentadienyl)zirconiumdibenzyl,
 bis(t-butylcyclopentadienyl)zirconiumdimethyl,
 bis(ethyltetramethylcyclopentadienyl)zirconiumdimethyl,
 bis(methylpropylcyclopentadienyl)zirconiumdibenzyl,
 35 bis(trimethylsilylcyclopentadienyl)zirconiumdibenzyl,

- dimethylsilylbis(cyclopentadienyl)zirconiumdimethyl,
 dimethylsilylbis(tetramethylcyclopentadienyl)titanium (III) allyl
 dimethylsilylbis(t-butylcyclopentadienyl)zirconiumdichloride,
 dimethylsilylbis(n-butylcyclopentadienyl)zirconiumdichloride,
 5 (methylenebis(tetramethylcyclopentadienyl)titanium(III) 2-(dimethylamino)benzyl,
 (methylenebis(n-butylcyclopentadienyl)titanium(III) 2-(dimethylamino)benzyl,
 dimethylsilylbis(indenyl)zirconiumbenzylchloride,
 dimethylsilylbis(2-methylindenyl)zirconiumdimethyl,
 dimethylsilylbis(2-methyl-4-phenylindenyl)zirconiumdimethyl,
 10 dimethylsilylbis(2-methylindenyl)zirconium-1,4-diphenyl-1,3-butadiene,
 dimethylsilylbis(2-methyl-4-phenylindenyl)zirconium (II) 1,4-diphenyl-1,3-butadiene,
 dimethylsilylbis(tetrahydroindenyl)zirconium(II) 1,4-diphenyl-1,3-butadiene,
 dimethylsilylbis(tetramethylcyclopentadienyl)zirconium dimethyl
 dimethylsilylbis(fluorenyl)zirconiumdimethyl,
 15 dimethylsilyl-bis(tetrahydrofluorenyl)zirconium bis(trimethylsilyl),
 (isopropylidene)(cyclopentadienyl)(fluorenyl)zirconiumdibenzyl, and
 dimethylsilyl(tetramethylcyclopentadienyl)(fluorenyl)zirconium dimethyl.

A further class of metal complexes utilized in the present invention corresponds to the preceding formula: MKZ_zX_x , or a dimer thereof, wherein M, K, X, x and z are as previously
 20 defined, and Z is a substituent of up to 50 non-hydrogen atoms that together with K forms a metallocycle with M.

Preferred Z substituents include groups containing up to 30 non-hydrogen atoms comprising at least one atom that is oxygen, sulfur, boron or a member of Group 14 of the Periodic Table of the Elements directly attached to K, and a different atom, selected from the group consisting of
 25 nitrogen, phosphorus, oxygen or sulfur that is covalently bonded to M.

More specifically this class of Group 4 metal complexes used according to the present invention includes "constrained geometry catalysts" corresponding to the formula:



wherein:

- 30 M is titanium or zirconium, preferably titanium in the +2, +3, or +4 formal oxidation state;
 K^1 is a delocalized, π -bonded ligand group optionally substituted with from 1 to 5 R^2 groups,

R^2 in each occurrence independently is selected from the group consisting of hydrogen, hydrocarbyl, silyl, germyl, cyano, halo and combinations thereof, said R^2 having up to 20 non-hydrogen atoms, or adjacent R^2 groups together form a divalent derivative (that is, a hydrocarbadiyl, siladiyl or germadiyl group) thereby forming a fused ring system,

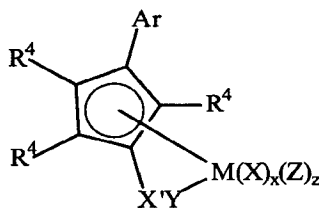
- 5 each X is a halo, hydrocarbyl, hydrocarbyloxy or silyl group, said group having up to 20 non-hydrogen atoms, or two X groups together form a neutral C_{5-30} conjugated diene or a divalent derivative thereof;

Y is -O-, -S-, -NR'-, -PR'-; and

X' is SiR'_2 , CR'_2 , $SiR'_2SiR'_2$, $CR'_2CR'_2$, $CR'=CR'$, $CR'_2SiR'_2$, or GeR'_2 , and

- 10 R' independently each occurrence is hydrogen or a group selected from silyl, hydrocarbyl, hydrocarbyloxy and combinations thereof, said R' having up to 30 carbon or silicon atoms.

Specific examples of the foregoing constrained geometry metal complexes include compounds corresponding to the formula:



- 15 wherein,

Ar is an aryl group of from 6 to 30 atoms not counting hydrogen;

- R^4 independently each occurrence is hydrogen, Ar, or a group other than Ar selected from hydrocarbyl, trihydrocarbylsilyl, trihydrocarbylgermyl, halide, hydrocarbyloxy, trihydrocarbylsiloxy, bis(trihydrocarbylsilyl)amino, di(hydrocarbyl)amino, hydrocarbadiylamino, hydrocarbylimino, di(hydrocarbyl)phosphino, hydrocarbadiylphosphino, hydrocarbylsulfido, halo-substituted hydrocarbyl, hydrocarbyloxy- substituted hydrocarbyl, trihydrocarbylsilyl- substituted hydrocarbyl, trihydrocarbylsiloxy- substituted hydrocarbyl, bis(trihydrocarbylsilyl)amino-substituted hydrocarbyl, di(hydrocarbyl)amino- substituted hydrocarbyl, hydrocarbyleneamino-substituted hydrocarbyl, di(hydrocarbyl)phosphino- substituted hydrocarbyl, hydrocarbylenephosphino- substituted hydrocarbyl, or hydrocarbylsulfido- substituted hydrocarbyl, said R group having up to 40 atoms not counting hydrogen atoms;

M is titanium;

X' is SiR^6_2 , CR^6_2 , $SiR^6_2SiR^6_2$, $CR^6_2CR^6_2$, $CR^6=CR^6$, $CR^6_2SiR^6_2$, BR^6 , BR^6L'' , or GeR^6_2 ;

Y is -O-, -S-, -NR⁵-, -PR⁵-; -NR⁵₂, or -PR⁵₂;

R^5 , independently each occurrence, is hydrocarbyl, trihydrocarbylsilyl, or trihydrocarbylsilylhydrocarbyl, said R^5 having up to 20 atoms other than hydrogen, and optionally two R^5 groups or R^5 together with Y or Z form a ring system;

R^6 , independently each occurrence, is hydrogen, or a member selected from hydrocarbyl, hydrocarbyloxy, silyl, halogenated alkyl, halogenated aryl, $-NR^5_2$, and combinations thereof, said R^6 having up to 20 non-hydrogen atoms, and optionally, two R^6 groups or R^6 together with Z forms a ring system;

Z is a neutral diene or a monodentate or polydentate Lewis base optionally bonded to R^5 , R^6 , or X;

X is hydrogen, a monovalent anionic ligand group having up to 60 atoms not counting hydrogen, or two X groups are a divalent ligand group;

x is 1 or 2; and

z is 0, 1 or 2.

Preferred examples of the foregoing metal complexes are substituted at both the 3- and 4-positions of a cyclopentadienyl or indenyl group with an Ar group.

Examples of the foregoing metal complexes include:

(3-phenylcyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dichloride,

(3-phenylcyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dimethyl,

(3-phenylcyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium (II) 1,3-diphenyl-1,3-

butadiene;

(3-(pyrrol-1-yl)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dichloride,

(3-(pyrrol-1-yl)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dimethyl,

(3-(pyrrol-1-yl)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium (II) 1,4-

diphenyl-1,3-butadiene;

(3-(1-methylpyrrol-3-yl)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dichloride,

(3-(1-methylpyrrol-3-yl)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dimethyl,

(3-(1-methylpyrrol-3-yl)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium (II) 1,4-

diphenyl-1,3-butadiene;

(3,4-diphenylcyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dichloride,

(3,4-diphenylcyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dimethyl,

(3,4-diphenylcyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium (II) 1,3-

pentadiene;

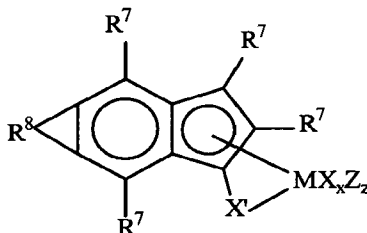
(3-(3-N,N-dimethylamino)phenyl)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dichloride,

(3-(3-N,N-dimethylamino)phenyl)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium

- dimethyl,
 (3-(3-N,N-dimethylamino)phenylcyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium
 (II) 1,4-diphenyl-1,3-butadiene;
 (3-(4-methoxyphenyl)-4-methylcyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium
 5 dichloride,
 (3-(4-methoxyphenyl)-4-phenylcyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dimethyl,
 (3-(4-methoxyphenyl)-4-phenylcyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium (II)
 1,4-diphenyl-1,3-butadiene;
 (3-phenyl-4-methoxycyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dichloride,
 10 (3-phenyl-4-methoxycyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dimethyl,
 (3-phenyl-4-methoxycyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium (II) 1,4-
 diphenyl-1,3-butadiene;
 (3-phenyl-4-(N,N-dimethylamino)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium
 dichloride,
 15 (3-phenyl-4-(N,N-dimethylamino)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium
 dimethyl,
 (3-phenyl-4-(N,N-dimethylamino)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium
 (II) 1,4-diphenyl-1,3-butadiene;
 2-methyl-(3,4-di(4-methylphenyl)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium
 20 dichloride,
 2-methyl-(3,4-di(4-methylphenyl)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium
 dimethyl,
 2-methyl-(3,4-di(4-methylphenyl)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium
 (II) 1,4-diphenyl-1,3-butadiene;
 25 ((2,3-diphenyl)-4-(N,N-dimethylamino)cyclopentadien-1-yl)dimethyl(t-butylamido)silane
 titanium dichloride,
 ((2,3-diphenyl)-4-(N,N-dimethylamino)cyclopentadien-1-yl)dimethyl(t-butylamido)silane
 titanium dimethyl,
 ((2,3-diphenyl)-4-(N,N-dimethylamino)cyclopentadien-1-yl)dimethyl(t-
 30 butylamido)silanetitanium (II) 1,4-diphenyl-1,3-butadiene;
 (2,3,4-triphenyl-5-methylcyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dichloride,
 (2,3,4-triphenyl-5-methylcyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dimethyl,
 (2,3,4-triphenyl-5-methylcyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium (II) 1,4-
 diphenyl-1,3-butadiene;
 35 (3-phenyl-4-methoxycyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dichloride,

(3-phenyl-4-methoxycyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dimethyl,
 (3-phenyl-4-methoxycyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium (II) 1,4-
 diphenyl-1,3-butadiene;
 (2,3-diphenyl-4-(n-butyl)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dichloride,
 5 (2,3-diphenyl-4-(n-butyl)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dimethyl,
 (2,3-diphenyl-4-(n-butyl)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium (II) 1,4-
 diphenyl-1,3-butadiene;
 (2,3,4,5-tetraphenylcyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dichloride,
 (2,3,4,5-tetraphenylcyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dimethyl, and
 10 (2,3,4,5-tetraphenylcyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium (II) 1,4-
 diphenyl-1,3-butadiene.

Additional examples of suitable metal complexes for use as catalyst (A) herein are polycyclic complexes corresponding to the formula:

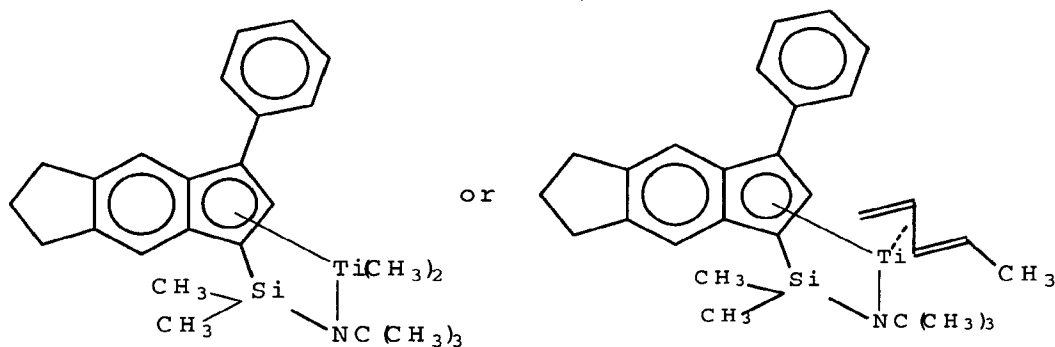


15 where M is titanium in the +2, +3 or +4 formal oxidation state;
 R^7 independently each occurrence is hydride, hydrocarbyl, silyl, germyl, halide, hydrocarbyloxy, hydrocarbylsiloxy, hydrocarbylsilylamino, di(hydrocarbyl)amino, hydrocarbyleneamino, di(hydrocarbyl)phosphino, hydrocarbylene-phosphino, hydrocarbylsulfido, halo-substituted hydrocarbyl, hydrocarbyloxy-substituted hydrocarbyl, silyl-substituted
 20 hydrocarbyl, hydrocarbylsiloxy-substituted hydrocarbyl, hydrocarbylsilylamino-substituted hydrocarbyl, di(hydrocarbyl)amino-substituted hydrocarbyl, hydrocarbyleneamino-substituted hydrocarbyl, di(hydrocarbyl)phosphino-substituted hydrocarbyl, hydrocarbylene-phosphino-substituted hydrocarbyl, or hydrocarbylsulfido-substituted hydrocarbyl, said R^7 group having up to 40 atoms not counting hydrogen, and optionally two or more of the foregoing groups may together
 25 form a divalent derivative;
 R^8 is a divalent hydrocarbylene- or substituted hydrocarbylene group forming a fused system with the remainder of the metal complex, said R^8 containing from 1 to 30 atoms not counting hydrogen;
 X' is a divalent moiety, or a moiety comprising one σ -bond and a neutral two electron pair
 30 able to form a coordinate-covalent bond to M, said X' comprising boron, or a member of Group 14 of the Periodic Table of the Elements, and also comprising nitrogen, phosphorus, sulfur or oxygen;

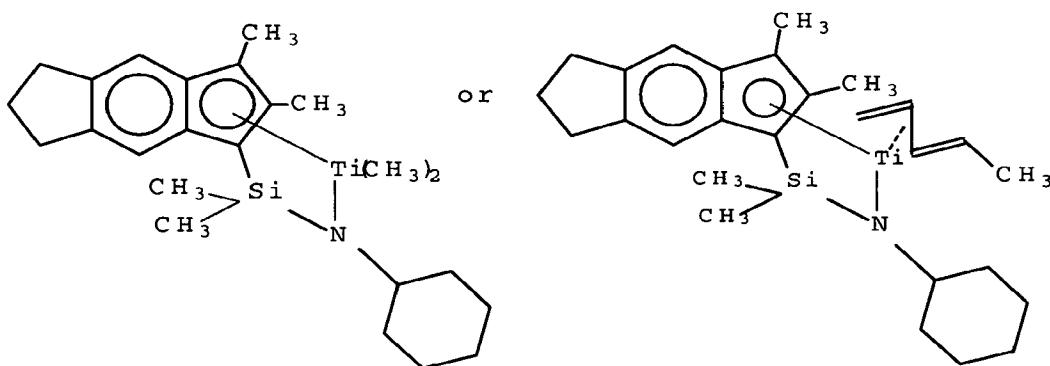
X is a monovalent anionic ligand group having up to 60 atoms exclusive of the class of ligands that are cyclic, delocalized, π -bound ligand groups and optionally two X groups together form a divalent ligand group;

- 5 Z independently each occurrence is a neutral ligating compound having up to 20 atoms;
 x is 0, 1 or 2; and
 z is zero or 1.

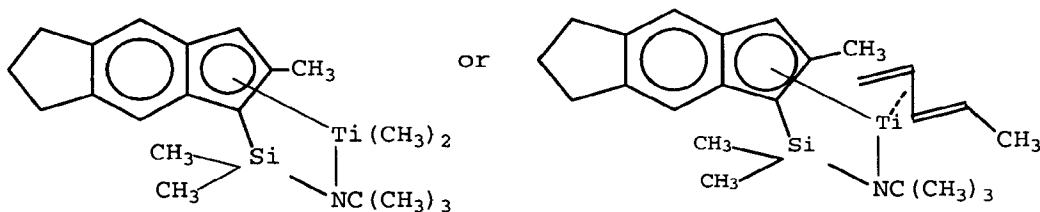
Preferred examples of such complexes are 3-phenyl-substituted s-indecenyl complexes corresponding to the formula:



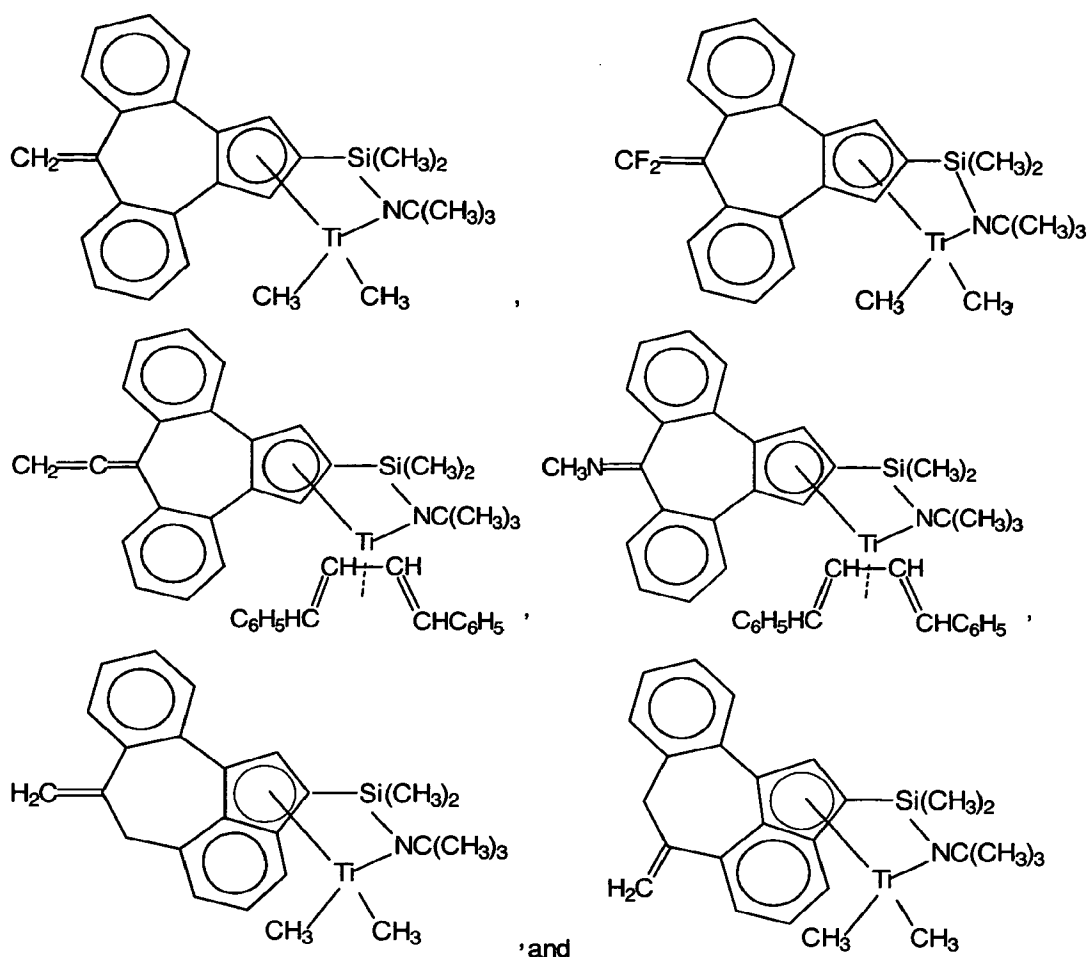
- 10 2,3-dimethyl-substituted s-indecenyl complexes corresponding to the formulas:



or 2-methyl-substituted s-indecenyl complexes corresponding to the formula:



- 15 Additional examples of metal complexes that are usefully employed as catalyst (A) according to the present invention include those of the formula:



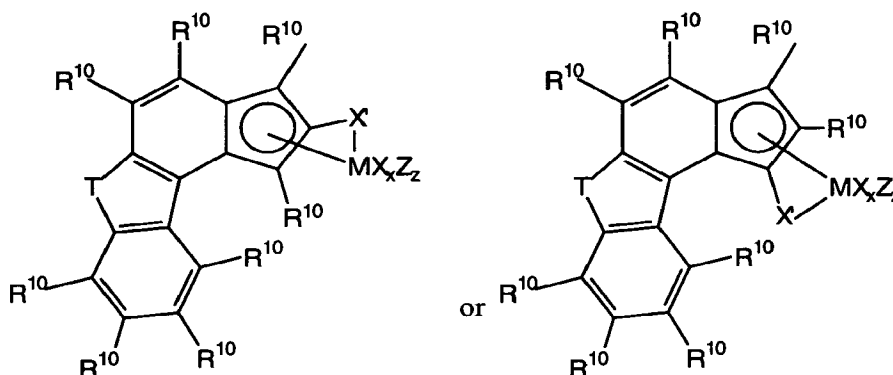
Specific metal complexes include:

- 5 (8-methylene-1,8-dihydrodibenzo[*e,h*]azulen-1-yl)-N-(1,1-dimethylethyl)dimethylsilylamide titanium (II) 1,4-diphenyl-1,3-butadiene,
- (8-methylene-1,8-dihydrodibenzo[*e,h*]azulen-1-yl)-N-(1,1-dimethylethyl)dimethylsilylamide titanium (II) 1,3-pentadiene,
- (8-methylene-1,8-dihydrodibenzo[*e,h*]azulen-1-yl)-N-(1,1-dimethylethyl)dimethylsilylamide titanium (III) 2-(N,N-dimethylamino)benzyl,
- 10 (8-methylene-1,8-dihydrodibenzo[*e,h*]azulen-1-yl)-N-(1,1-dimethylethyl)dimethylsilylamide titanium (IV) dichloride,
- (8-methylene-1,8-dihydrodibenzo[*e,h*]azulen-1-yl)-N-(1,1-dimethylethyl)dimethylsilylamide titanium (IV) dimethyl,
- 15 (8-methylene-1,8-dihydrodibenzo[*e,h*]azulen-1-yl)-N-(1,1-dimethylethyl)dimethylsilylamide titanium (IV) dibenzyl,

- (8-difluoromethylene-1,8-dihydrodibenzo[*e,h*]azulen-1-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (II) 1,4-diphenyl-1,3-butadiene,
 (8-difluoromethylene-1,8-dihydrodibenzo[*e,h*]azulen-1-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (II) 1,3-pentadiene,
 5 (8-difluoromethylene-1,8-dihydrodibenzo[*e,h*]azulen-1-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (III) 2-(N,N-dimethylamino)benzyl,
 (8-difluoromethylene-1,8-dihydrodibenzo[*e,h*]azulen-1-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (IV) dichloride,
 (8-difluoromethylene-1,8-dihydrodibenzo[*e,h*]azulen-1-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (IV) dimethyl,
 10 (8-difluoromethylene-1,8-dihydrodibenzo[*e,h*]azulen-1-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (IV) dibenzyl,
- (8-methylene-1,8-dihydrodibenzo[*e,h*]azulen-2-yl)-N-(1,1-dimethylethyl)dimethylsilanamide
 15 titanium (II) 1,4-diphenyl-1,3-butadiene,
 (8-methylene-1,8-dihydrodibenzo[*e,h*]azulen-2-yl)-N-(1,1-dimethylethyl)dimethylsilanamide
 titanium (II) 1,3-pentadiene,
 (8-methylene-1,8-dihydrodibenzo[*e,h*]azulen-2-yl)-N-(1,1-dimethylethyl)dimethylsilanamide
 titanium (III) 2-(N,N-dimethylamino)benzyl,
 20 (8-methylene-1,8-dihydrodibenzo[*e,h*]azulen-2-yl)-N-(1,1-dimethylethyl)dimethylsilanamide
 titanium (IV) dichloride,
 (8-methylene-1,8-dihydrodibenzo[*e,h*]azulen-2-yl)-N-(1,1-dimethylethyl)dimethylsilanamide
 titanium (IV) dimethyl,
 (8-methylene-1,8-dihydrodibenzo[*e,h*]azulen-2-yl)-N-(1,1-dimethylethyl)dimethylsilanamide
 25 titanium (IV) dibenzyl,
- (8-difluoromethylene-1,8-dihydrodibenzo[*e,h*]azulen-2-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (II) 1,4-diphenyl-1,3-butadiene,
 (8-difluoromethylene-1,8-dihydrodibenzo[*e,h*]azulen-2-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (II) 1,3-pentadiene,
 30 (8-difluoromethylene-1,8-dihydrodibenzo[*e,h*]azulen-2-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (III) 2-(N,N-dimethylamino)benzyl,
 (8-difluoromethylene-1,8-dihydrodibenzo[*e,h*]azulen-2-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (IV) dichloride,

(8-difluoromethylene-1,8-dihydrodibenzo[*e,h*]azulen-2-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (IV) dimethyl, (8-difluoromethylene-1,8-dihydrodibenzo[*e,h*]azulen-2-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (IV) dibenzyl, and mixtures thereof, especially mixtures of positional isomers.

Further illustrative examples of metal complexes for use according to the present invention correspond to the formula:



where M is titanium in the +2, +3 or +4 formal oxidation state;

T_i is -NR⁹- or -O-;

R⁹ is hydrocarbyl, silyl, germyl, dihydrocarbylboryl, or halohydrocarbyl or up to 10 atoms not counting hydrogen;

R¹⁰ independently each occurrence is hydrogen, hydrocarbyl, trihydrocarbylsilyl, trihydrocarbylsilylhydrocarbyl, germyl, halide, hydrocarbyloxy, hydrocarbylsiloxy, hydrocarbylsilylamino, di(hydrocarbyl)amino, hydrocarbyleneamino, di(hydrocarbyl)phosphino, hydrocarbylene-phosphino, hydrocarbylsulfido, halo- substituted hydrocarbyl, hydrocarbyloxy-substituted hydrocarbyl, silyl- substituted hydrocarbyl, hydrocarbylsiloxy- substituted hydrocarbyl, hydrocarbylsilylamino- substituted hydrocarbyl, di(hydrocarbyl)amino- substituted hydrocarbyl, hydrocarbyleneamino-substituted hydrocarbyl, di(hydrocarbyl)phosphino- substituted hydrocarbyl, hydrocarbylenephosphino- substituted hydrocarbyl, or hydrocarbylsulfido- substituted hydrocarbyl, said R¹⁰ group having up to 40 atoms not counting hydrogen atoms, and optionally two or more of the foregoing adjacent R¹⁰ groups may together form a divalent derivative thereby forming a saturated or unsaturated fused ring;

X' is a divalent moiety lacking in delocalized π -electrons, or such a moiety comprising one σ -bond and a neutral two electron pair able to form a coordinate-covalent bond to M, said X' comprising boron, or a member of Group 14 of the Periodic Table of the Elements, and also comprising nitrogen, phosphorus, sulfur or oxygen;

X is a monovalent anionic ligand group having up to 60 atoms exclusive of the class of ligands that are cyclic ligand groups bound to M through delocalized π -electrons or two X groups together are a divalent anionic ligand group;

Z independently each occurrence is a neutral ligating compound having up to 20 atoms;

5 x is 0, 1, 2, or 3; and

z is 0 or 1.

Highly preferably T is $=N(CH_3)$, X is halo or hydrocarbyl, x is 2, X' is dimethylsilane, z is 0, and R^{10} each occurrence is hydrogen, a hydrocarbyl, hydrocarbyloxy, dihydrocarbylamino, hydrocarbyleneamino, dihydrocarbylamino- substituted hydrocarbyl group, or

10 hydrocarbyleneamino- substituted hydrocarbyl group of up to 20 atoms not counting hydrogen, and optionally two R^{10} groups may be joined together.

Illustrative metal complexes of the foregoing formula that may be employed in the practice of the present invention further include the following compounds:

(t-butylamido)dimethyl-[6,7]benzo-[4,5:2',3'] (1-methylisoindol)-(3H)-indene-2-yl)silanetitanium

15 (II) 1,4-diphenyl-1,3-butadiene,

(t-butylamido)dimethyl-[6,7]benzo-[4,5:2',3'] (1-methylisoindol)-(3H)-indene-2-yl)silanetitanium

(II) 1,3-pentadiene,

(t-butylamido)dimethyl-[6,7]benzo-[4,5:2',3'] (1-methylisoindol)-(3H)-indene-2-yl)silanetitanium

(III) 2-(N,N-dimethylamino)benzyl,

20 (t-butylamido)dimethyl-[6,7]benzo-[4,5:2',3'] (1-methylisoindol)-(3H)-indene-2-yl)silanetitanium

(IV) dichloride,

(t-butylamido)dimethyl-[6,7]benzo-[4,5:2',3'] (1-methylisoindol)-(3H)-indene-2-yl)silanetitanium

(IV) dimethyl,

(t-butylamido)dimethyl-[6,7]benzo-[4,5:2',3'] (1-methylisoindol)-(3H)-indene-2-yl)silanetitanium

25 (IV) dibenzyl,

(t-butylamido)dimethyl-[6,7]benzo-[4,5:2',3'] (1-methylisoindol)-(3H)-indene-2-yl)silanetitanium

(IV) bis(trimethylsilyl),

(cyclohexylamido)dimethyl-[6,7]benzo-[4,5:2',3'] (1-methylisoindol)-(3H)-indene-2-

30 yl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,

(cyclohexylamido)dimethyl-[6,7]benzo-[4,5:2',3'] (1-methylisoindol)-(3H)-indene-2-

yl)silanetitanium (II) 1,3-pentadiene,

(cyclohexylamido)dimethyl-[6,7]benzo-[4,5:2',3'] (1-methylisoindol)-(3H)-indene-2-

yl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,

- (cyclohexylamido)dimethyl-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (IV) dichloride,
 (cyclohexylamido)dimethyl-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (IV) dimethyl,
 5 (cyclohexylamido)dimethyl-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (IV) dibenzyl,
 (cyclohexylamido)dimethyl-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (IV) bis(trimethylsilyl),
- 10 (t-butylamido)di(p-methylphenyl)-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
 (t-butylamido)di(p-methylphenyl)-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (II) 1,3-pentadiene,
 (t-butylamido)di(p-methylphenyl)-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
 15 (t-butylamido)di(p-methylphenyl)-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (IV) dichloride,
 (t-butylamido)di(p-methylphenyl)-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (IV) dimethyl,
- 20 (t-butylamido)di(p-methylphenyl)-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (IV) dibenzyl,
 (t-butylamido)di(p-methylphenyl)-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (IV) bis(trimethylsilyl),
- 25 (cyclohexylamido)di(p-methylphenyl)-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
 (cyclohexylamido)di(p-methylphenyl)-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (II) 1,3-pentadiene,
 (cyclohexylamido)di(p-methylphenyl)-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
 30 (cyclohexylamido)di(p-methylphenyl)-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (IV) dichloride,
 (cyclohexylamido)di(p-methylphenyl)-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (IV) dimethyl,

(cyclohexylamido)di(p-methylphenyl)-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (IV) dibenzyl; and
 (cyclohexylamido)di(p-methylphenyl)-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (IV) bis(trimethylsilyl).

5 Illustrative Group 4 metal complexes that may be employed in the practice of the present invention further include:

(tert-butylamido)(1,1-dimethyl-2,3,4,9,10-η-1,4,5,6,7,8-

hexahydronaphthalenyl)dimethylsilanetitaniumdimethyl,

(tert-butylamido)(1,1,2,3-tetramethyl-2,3,4,9,10-η-1,4,5,6,7,8-

10 hexahydronaphthalenyl)dimethylsilanetitaniumdimethyl,

(tert-butylamido)(tetramethyl-η⁵-cyclopentadienyl) dimethylsilanetitanium dibenzyl,

(tert-butylamido)(tetramethyl-η⁵-cyclopentadienyl)dimethylsilanetitanium dimethyl,

(tert-butylamido)(tetramethyl-η⁵-cyclopentadienyl)-1,2-ethanediyltitanium dimethyl,

(tert-butylamido)(tetramethyl-η⁵-indenyl)dimethylsilanetitanium dimethyl,

15 (tert-butylamido)(tetramethyl-η⁵-cyclopentadienyl)dimethylsilane titanium (III)

2-(dimethylamino)benzyl;

(tert-butylamido)(tetramethyl-η⁵-cyclopentadienyl)dimethylsilanetitanium (III) allyl,

(tert-butylamido)(tetramethyl-η⁵-cyclopentadienyl)dimethylsilanetitanium (III)

2,4-dimethylpentadienyl,

20 (tert-butylamido)(tetramethyl-η⁵-cyclopentadienyl)dimethylsilanetitanium (II)

1,4-diphenyl-1,3-butadiene,

(tert-butylamido)(tetramethyl-η⁵-cyclopentadienyl)dimethylsilanetitanium (II)

1,3-pentadiene,

(tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (II) 1,4-diphenyl-1,3-

25 butadiene,

(tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (II) 2,4-hexadiene,

(tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (IV) 2,3-dimethyl-1,3-

butadiene,

(tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (IV) isoprene,

30 (tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (IV) 1,3-butadiene,

(tert-butylamido)(2,3-dimethylindenyl)dimethylsilanetitanium (IV)

2,3-dimethyl-1,3-butadiene,

(tert-butylamido)(2,3-dimethylindenyl)dimethylsilanetitanium (IV)

isoprene

35 (tert-butylamido)(2,3-dimethylindenyl)dimethylsilanetitanium (IV) dimethyl

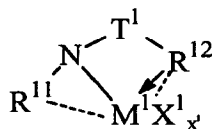
- (tert-butylamido)(2,3-dimethylindenyl)dimethylsilanetitanium (IV) dibenzyl
 (tert-butylamido)(2,3-dimethylindenyl)dimethylsilanetitanium (IV) 1,3-butadiene,
 (tert-butylamido)(2,3-dimethylindenyl)dimethylsilanetitanium (II) 1,3-pentadiene,
 (tert-butylamido)(2,3-dimethylindenyl)dimethylsilanetitanium (II) 1,4-diphenyl-
 5 1,3-butadiene,
 (tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (II) 1,3-pentadiene,
 (tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (IV) dimethyl,
 (tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (IV) dibenzyl,
 (tert-butylamido)(2-methyl-4-phenylindenyl)dimethylsilanetitanium (II)
 10 1,4-diphenyl-1,3-butadiene,
 (tert-butylamido)(2-methyl-4-phenylindenyl)dimethylsilanetitanium (II) 1,3-pentadiene,
 (tert-butylamido)(2-methyl-4-phenylindenyl)dimethylsilanetitanium (II) 2,4-hexadiene,
 (tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl)dimethyl- silanetitanium (IV)
 1,3-butadiene,
 15 (tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl)dimethylsilanetitanium (IV)
 2,3-dimethyl-1,3-butadiene,
 (tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl)dimethylsilanetitanium (IV)
 isoprene,
 (tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl)dimethyl- silanetitanium (II)
 20 1,4-dibenzyl-1,3-butadiene,
 (tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl)dimethylsilanetitanium (II)
 2,4-hexadiene,
 (tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl)dimethyl- silanetitanium (II)
 3-methyl-1,3-pentadiene,
 25 (tert-butylamido)(2,4-dimethylpentadien-3-yl)dimethylsilanetitaniumdimethyl,
 (tert-butylamido)(6,6-dimethylcyclohexadienyl)dimethylsilanetitaniumdimethyl,
 (tert-butylamido)(1,1-dimethyl-2,3,4,9,10- η -1,4,5,6,7,8-hexahydronaphthalen-4-
 yl)dimethylsilanetitaniumdimethyl,
 (tert-butylamido)(1,1,2,3-tetramethyl-2,3,4,9,10- η -1,4,5,6,7,8-hexahydronaphthalen-4-
 30 yl)dimethylsilanetitaniumdimethyl
 (tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl methylphenylsilanetitanium (IV)
 dimethyl,
 (tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl methylphenylsilanetitanium (II)
 1,4-diphenyl-1,3-butadiene,
 35 1-(tert-butylamido)-2-(tetramethyl- η^5 -cyclopentadienyl)ethanediyltitanium (IV)

dimethyl, and

1-(tert-butylamido)-2-(tetramethyl- η^5 -cyclopentadienyl)ethanediyl-titanium (II) 1,4-diphenyl-1,3-butadiene.

Other delocalized, π -bonded complexes, especially those containing other Group 4 metals, will, of course, be apparent to those skilled in the art, and are disclosed among other places in: WO 03/78480, WO 03/78483, WO 02/92610, WO 02/02577, US 2003/0004286 and US Patents 6,515,155, 6,555,634, 6,150,297, 6,034,022, 6,268,444, 6,015,868, 5,866,704, and 5,470,993.

The polyvalent Lewis base complexes for use in the present invention also include Group 4 metal derivatives, especially hafnium derivatives of hydrocarbylamine substituted heteroaryl compounds, especially compounds of the formula $R^{11}HN-T-R^{12}$. Preferably the complexes correspond to the formula:



wherein:

R^{11} is selected from alkyl, cycloalkyl, heteroalkyl, cycloheteroalkyl, aryl, and inertly substituted derivatives thereof containing from 1 to 30 atoms not counting hydrogen;

T^1 is a divalent bridging group of from 1 to 20 atoms other than hydrogen, preferably a mono- or di- C_{1-20} hydrocarbyl substituted methylene or silane group; and

R^{12} is a C_{6-20} heteroaryl group containing Lewis base functionality, especially a pyridin-2-yl- or substituted pyridin-2-yl group;

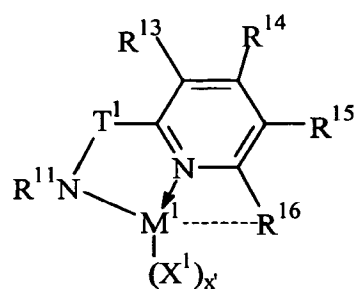
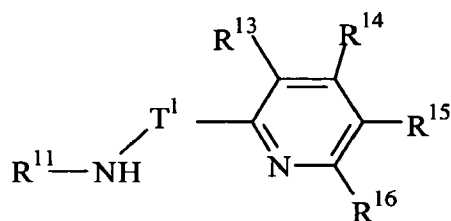
and in the metal complex, M^1 is a Group 4 metal, preferably hafnium;

X^1 is an anionic, neutral or dianionic ligand group;

x' is a number from 0 to 5 indicating the number of such X^1 groups; and

bonds, optional bonds and electron donative interactions are represented by lines, dotted lines and arrows respectively.

Preferred complexes are those wherein ligand formation results from hydrogen elimination from the amine group and optionally from the loss of one or more additional groups, especially from R^{12} . In addition, electron donation from the Lewis base functionality, preferably an electron pair, provides additional stability to the metal center. Preferred examples of the foregoing polyfunctional Lewis base compounds and the resulting metal complexes correspond to the formulas:

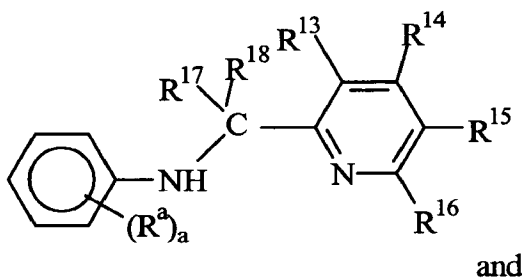


, wherein

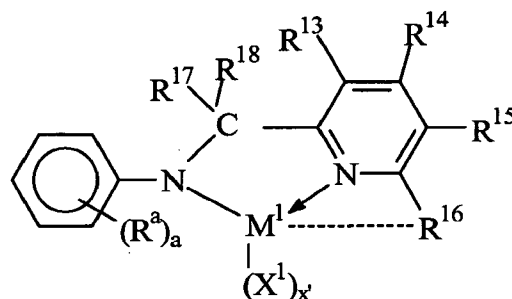
M^1 , X^1 , x' , R^{11} and T^1 are as previously defined,

- R^{13} , R^{14} , R^{15} and R^{16} are hydrogen, halo, or an alkyl, cycloalkyl, heteroalkyl, heterocycloalkyl, aryl, or silyl group of up to 20 atoms not counting hydrogen, or adjacent R^{13} , R^{14} , R^{15} or R^{16} groups may be joined together thereby forming fused ring derivatives, and bonds, optional bonds and electron pair donative interactions are represented by lines, dotted lines and arrows respectively.

More preferred examples of the foregoing difunctional Lewis base compounds and metal complexes correspond to the formula:



and



10

wherein

M^1 , X^1 , and x' are as previously defined,

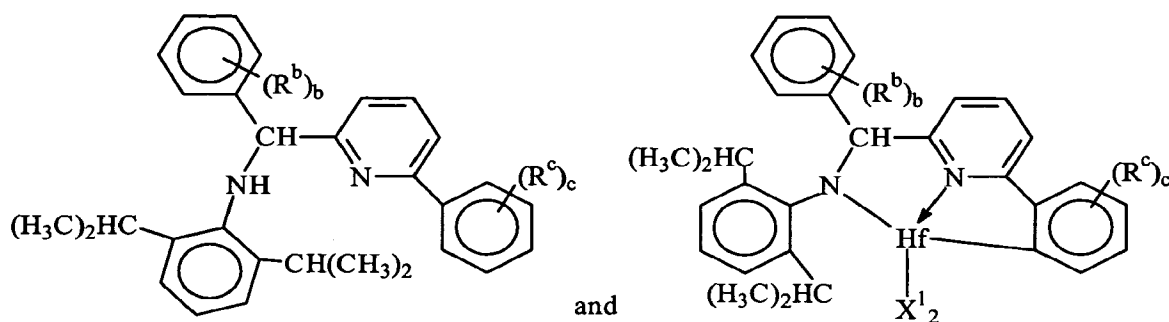
R^{13} , R^{14} , R^{15} and R^{16} are as previously defined, preferably R^{13} , R^{14} , and R^{15} are hydrogen, or C_{1-4} alkyl, and R^{16} is C_{6-20} aryl, most preferably naphthalenyl;

- R^a independently each occurrence is C_{1-4} alkyl, and a is 1-5, most preferably R^a in two ortho- positions is isopropyl or t-butyl;

R^{17} and R^{18} independently each occurrence are hydrogen, halogen, or a C_{1-20} alkyl or aryl group, most preferably one of R^{17} and R^{18} is hydrogen and the other is a C_{6-20} aryl group, especially a fused polycyclic aryl group, most preferably an anthracenyl group, and

- bonds, optional bonds and electron pair donative interactions are represented by lines, dotted lines and arrows respectively.

Highly preferred polyfunctional Lewis base compounds and metal complexes for use herein as catalyst (A) correspond to the formula:

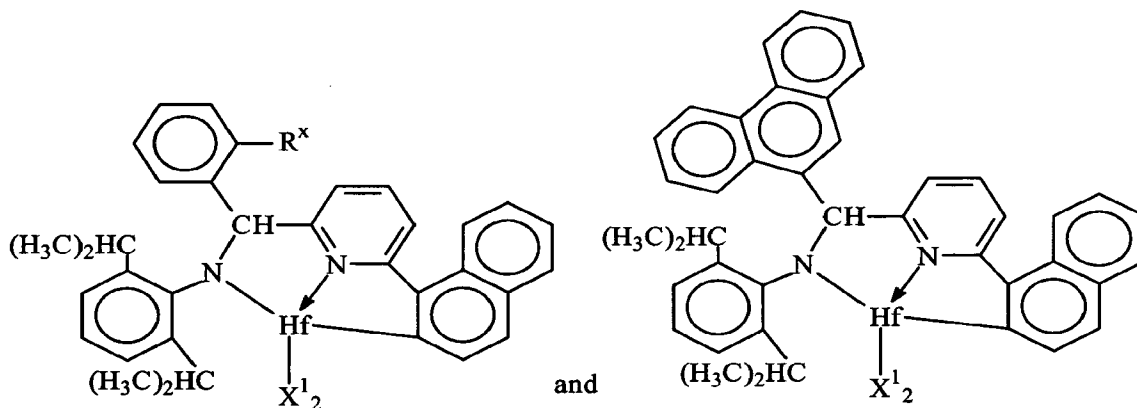


wherein X^1 each occurrence is halide, N,N-dimethylamido, or C_{1-4} alkyl, and preferably each occurrence X is methyl;

R^b independently each occurrence is hydrogen, halogen, C_{1-20} alkyl, or C_{6-20} aryl, or two adjacent R^b groups are joined together thereby forming a ring, and b is 1-5; and

R^c independently each occurrence is hydrogen, halogen, C_{1-20} alkyl, or C_{6-20} aryl, or two adjacent R^c groups are joined together thereby forming a ring, and c is 1-5.

Most highly preferred examples of metal complexes for use as catalyst (A) according to the present invention are complexes of the following formulas:



wherein R^x is C_{1-4} alkyl or cycloalkyl, preferably methyl or isopropyl; and

X^1 each occurrence is halide, N,N-dimethylamido, or C_{1-4} alkyl, preferably methyl.

Examples of metal complexes usefully employed as catalyst (A) according to the present invention include:

[N-(2,6-di(1-methylethyl)phenyl)amido](o-tolyl)(α -naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dimethyl;

[N-(2,6-di(1-methylethyl)phenyl)amido](o-tolyl)(α -naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium di(N,N-dimethylamido);

[N-(2,6-di(1-methylethyl)phenyl)amido](o-tolyl)(α -naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dichloride;

[N-(2,6-di(1-methylethyl)phenyl)amido)(2-isopropylphenyl)(α -naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dimethyl;

[N-(2,6-di(1-methylethyl)phenyl)amido)(2-isopropylphenyl)(α -naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium di(N,N-dimethylamido);

5 [N-(2,6-di(1-methylethyl)phenyl)amido)(2-isopropylphenyl)(α -naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dichloride;

[N-(2,6-di(1-methylethyl)phenyl)amido)(phenanthren-5-yl)(α -naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dimethyl;

10 [N-(2,6-di(1-methylethyl)phenyl)amido)(phenanthren-5-yl)(α -naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium di(N,N-dimethylamido); and

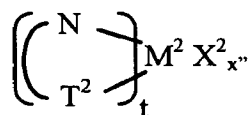
[N-(2,6-di(1-methylethyl)phenyl)amido)(phenanthren-5-yl)(α -naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dichloride.

Under the reaction conditions used to prepare the metal complexes used in the present invention, it has been discovered that the hydrogen of the 2-position of the α -naphthalene group substituted at the 6-position of the pyridin-2-yl group is subject to elimination, thereby uniquely
15 forming metal complexes wherein the metal is covalently bonded to both the resulting amide group and to the 2-position of the α -naphthalenyl group, as well as stabilized by coordination to the pyridinyl nitrogen atom through the electron pair of the nitrogen atom.

The foregoing polyvalent Lewis base complexes are conveniently prepared by standard
20 metallation and ligand exchange procedures involving a source of the Group 4 metal and the neutral polyfunctional ligand source. The complexes may also be prepared by means of an amide elimination and hydrocarbylation process starting from the corresponding Group 4 metal tetraamide and a hydrocarbylating agent, such as trimethylaluminum. Other techniques may be used as well. These complexes are known from the disclosures of, among others, US-A- 6,320,005,
25 US-A-6,103,657, WO 02/38628, WO 03/40195, and USSN 10/429024, filed May 2, 2003.

Suitable metal compounds for use as catalyst (B) include the foregoing metal compounds as well as other metal compounds, with the proviso that they incorporate comonomer relatively poorly compared to catalyst (A). Accordingly, in addition to the previously identified metal complexes the following additional metal complexes may be utilized.

30 Group 4-10 derivatives corresponding to the formula:



wherein

M^2 is a metal of Groups 4-10 of the Periodic Table of the elements, preferably Group 4, Ni(II) or Pd(II), most preferably zirconium;

T^2 is a nitrogen, oxygen or phosphorus containing group;

X^2 is halo, hydrocarbyl, or hydrocarbyloxy;

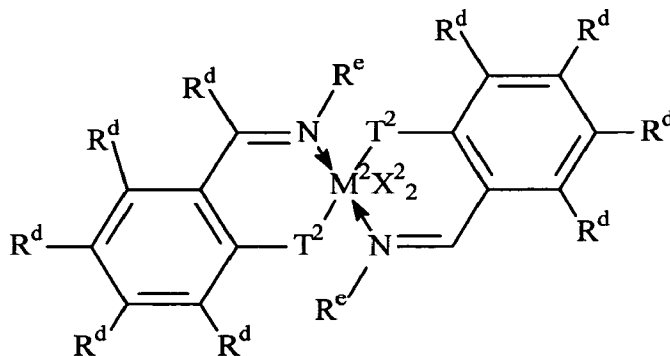
5 t is one or two;

x'' is a number selected to provide charge balance;

and T^2 and N are linked by a bridging ligand.

Such catalysts have been previously disclosed in J. Am. Chem. Soc., 118, 267-268 (1996),
J. Am. Chem. Soc., 117, 6414 -6415 (1995), and Organometallics, 16, 1514-1516, (1997), among
 10 other disclosures.

Preferred examples of the foregoing metal complexes for use as catalyst (B) are aromatic diimine or aromatic dioximine complexes of Group 4 metals, especially zirconium, corresponding to the formula:



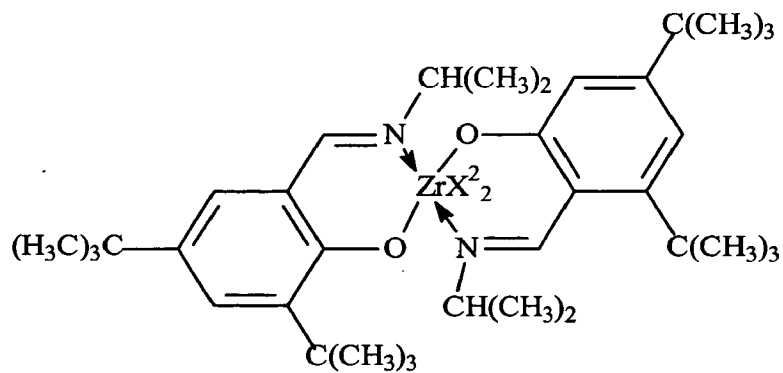
15 wherein;

M^2 , X^2 and T^2 are as previously defined;

R^d independently each occurrence is hydrogen, halogen, or R^e ; and

R^e independently each occurrence is C_{1-10} hydrocarbyl, preferably C_{1-4} alkyl.

Most preferred examples of the foregoing metal complexes for use as catalyst (B) are
 20 aromatic dioximine complexes of zirconium, corresponding to the formula:



wherein;

X^2 is as previously defined, preferably C_{1-10} hydrocarbyl, most preferably benzyl.

The foregoing complexes for use as catalyst (B) also include certain phosphinimine complexes are disclosed in EP-A-890581. These complexes correspond to the formula:

5 $[(R^f)_3-P=N]_fM(K^2)(R^f)_{3-f}$, wherein:

R^f is a monovalent ligand or two R^f groups together are a divalent ligand, preferably R^f is hydrogen or C_{1-4} alkyl;

M is a Group 4 metal,

10 K^2 is a group containing delocalized π -electrons through which K^2 is bound to M, said K^2 group containing up to 50 atoms not counting hydrogen atoms, and
f is 1 or 2.

Each of the metal complex catalysts (A) and (B) (also interchangeably referred to in the literature as precatalysts) may be activated to form the active catalyst composition by combination with a cocatalyst, preferably a cation forming cocatalyst, a strong Lewis acid, or a combination
15 thereof. In a preferred embodiment, the shuttling agent is employed both for purposes of chain transfer and as the optional strong acid cocatalyst component of the catalyst composition.

The metal complexes may also be rendered catalytically active by combination with a cation forming cocatalyst, such as those previously known in the art for use with Group 4 metal olefin polymerization complexes. Suitable cation forming cocatalysts for use herein include neutral
20 Lewis acids, such as C_{1-30} hydrocarbyl substituted Group 13 compounds, especially tri(hydrocarbyl)aluminum- or tri(hydrocarbyl)boron compounds and halogenated (including perhalogenated) derivatives thereof, having from 1 to 10 carbons in each hydrocarbyl or halogenated hydrocarbyl group, more especially perfluorinated tri(aryl)boron compounds, and most especially tris(pentafluoro-phenyl)borane; nonpolymeric, compatible, noncoordinating, ion forming
25 compounds (including the use of such compounds under oxidizing conditions), especially the use of ammonium-, phosphonium-, oxonium-, carbonium-, silylium- or sulfonium- salts of compatible, noncoordinating anions, or ferrocenium-, lead- or silver salts of compatible, noncoordinating anions; and combinations of the foregoing cation forming cocatalysts and techniques. The foregoing activating cocatalysts and activating techniques have been previously taught with respect
30 to different metal complexes for olefin polymerizations in the following references: EP-A-277,003, US-A-5,153,157, US-A-5,064,802, US-A-5,321,106, US-A-5,721,185, US-A-5,350,723, US-A-5,425,872, US-A-5,625,087, US-A-5,883,204, US-A-5,919,983, US-A-5,783,512, WO 99/15534, and WO99/42467.

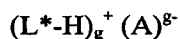
Combinations of neutral Lewis acids, especially the combination of a trialkyl aluminum
35 compound having from 1 to 4 carbons in each alkyl group and a halogenated tri(hydrocarbyl)boron

compound having from 1 to 20 carbons in each hydrocarbyl group, especially tris(pentafluorophenyl)borane, further combinations of such neutral Lewis acid mixtures with a polymeric or oligomeric alumoxane, and combinations of a single neutral Lewis acid, especially tris(pentafluorophenyl)borane with a polymeric or oligomeric alumoxane may be used as activating
 5 cocatalysts. Preferred molar ratios of metal complex:tris(pentafluorophenyl-borane:alumoxane are from 1:1:1 to 1:5:20, more preferably from 1:1:1.5 to 1:5:10.

Suitable ion forming compounds useful as cocatalysts in one embodiment of the present invention comprise a cation which is a Bronsted acid capable of donating a proton, and a compatible, noncoordinating anion, A^- . As used herein, the term "noncoordinating" means an anion
 10 or substance which either does not coordinate to the Group 4 metal containing precursor complex and the catalytic derivative derived therefrom, or which is only weakly coordinated to such complexes thereby remaining sufficiently labile to be displaced by a neutral Lewis base. A noncoordinating anion specifically refers to an anion which when functioning as a charge balancing anion in a cationic metal complex does not transfer an anionic substituent or fragment thereof to
 15 said cation thereby forming neutral complexes. "Compatible anions" are anions which are not degraded to neutrality when the initially formed complex decomposes and are noninterfering with desired subsequent polymerization or other uses of the complex.

Preferred anions are those containing a single coordination complex comprising a charge-bearing metal or metalloid core which anion is capable of balancing the charge of the active catalyst
 20 species (the metal cation) which may be formed when the two components are combined. Also, said anion should be sufficiently labile to be displaced by olefinic, diolefinic and acetylenically unsaturated compounds or other neutral Lewis bases such as ethers or nitriles. Suitable metals include, but are not limited to, aluminum, gold and platinum. Suitable metalloids include, but are not limited to, boron, phosphorus, and silicon. Compounds containing anions which comprise
 25 coordination complexes containing a single metal or metalloid atom are, of course, well known and many, particularly such compounds containing a single boron atom in the anion portion, are available commercially.

Preferably such cocatalysts may be represented by the following general formula:



30 wherein:

L^* is a neutral Lewis base;

$(L^*-H)^+$ is a conjugate Bronsted acid of L^* ;

A^{g-} is a noncoordinating, compatible anion having a charge of g^- , and

g is an integer from 1 to 3.

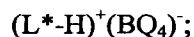
More preferably A^{8-} corresponds to the formula: $[M'Q_4]^-$;

wherein:

M' is boron or aluminum in the +3 formal oxidation state; and

Q independently each occurrence is selected from hydride, dialkylamido, halide,
 5 hydrocarbyl, hydrocarbyloxy, halosubstituted-hydrocarbyl, halosubstituted hydrocarbyloxy, and
 halo- substituted silylhydrocarbyl radicals (including perhalogenated hydrocarbyl- perhalogenated
 hydrocarbyloxy- and perhalogenated silylhydrocarbyl radicals), said Q having up to 20 carbons with
 the proviso that in not more than one occurrence is Q halide. Examples of suitable
 hydrocarbyloxy Q groups are disclosed in US-A-5,296,433.

10 In a more preferred embodiment, d is one, that is, the counter ion has a single negative
 charge and is A^- . Activating cocatalysts comprising boron which are particularly useful in the
 preparation of catalysts of this invention may be represented by the following general formula:



wherein:

15 L^* is as previously defined;

B is boron in a formal oxidation state of 3; and

Q is a hydrocarbyl-, hydrocarbyloxy-, fluorinated hydrocarbyl-, fluorinated
 hydrocarbyloxy-, or fluorinated silylhydrocarbyl- group of up to 20 nonhydrogen atoms, with the
 proviso that in not more than one occasion is Q hydrocarbyl.

20 Preferred Lewis base salts are ammonium salts, more preferably trialkylammonium salts
 containing one or more C_{12-40} alkyl groups. Most preferably, Q is each occurrence a fluorinated aryl
 group, especially, a pentafluorophenyl group.

Illustrative, but not limiting, examples of boron compounds which may be used as an
 activating cocatalyst in the preparation of the improved catalysts of this invention are
 25 tri-substituted ammonium salts such as:

trimethylammonium tetrakis(pentafluorophenyl) borate,
 triethylammonium tetrakis(pentafluorophenyl) borate,
 tripropylammonium tetrakis(pentafluorophenyl) borate,
 tri(n-butyl)ammonium tetrakis(pentafluorophenyl) borate,
 30 tri(sec-butyl)ammonium tetrakis(pentafluorophenyl) borate,
 N,N-dimethylanilinium tetrakis(pentafluorophenyl) borate,
 N,N-dimethylanilinium n-butyltris(pentafluorophenyl) borate,
 N,N-dimethylanilinium benzyltris(pentafluorophenyl) borate,
 N,N-dimethylanilinium tetrakis(4-(t-butyl)dimethylsilyl)-2, 3, 5, 6-tetrafluorophenyl) borate,
 35 N,N-dimethylanilinium tetrakis(4-(triisopropylsilyl)-2, 3, 5, 6-tetrafluorophenyl) borate,

N,N-dimethylanilinium pentafluorophenoxytris(pentafluorophenyl) borate,
 N,N-diethylanilinium tetrakis(pentafluorophenyl) borate,
 N,N-dimethyl-2,4,6-trimethylanilinium tetrakis(pentafluorophenyl) borate,
 dimethyloctadecylammonium tetrakis(pentafluorophenyl) borate,
 5 methyldioctadecylammonium tetrakis(pentafluorophenyl) borate,
 dialkyl ammonium salts such as:

di-(i-propyl)ammonium tetrakis(pentafluorophenyl) borate,
 methyloctadecylammonium tetrakis(pentafluorophenyl) borate,
 methyloctadodecylammonium tetrakis(pentafluorophenyl) borate, and
 10 dioctadecylammonium tetrakis(pentafluorophenyl) borate;
 tri-substituted phosphonium salts such as:

triphenylphosphonium tetrakis(pentafluorophenyl) borate,
 methyldioctadecylphosphonium tetrakis(pentafluorophenyl) borate, and
 tri(2,6-dimethylphenyl)phosphonium tetrakis(pentafluorophenyl) borate;

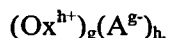
15 di-substituted oxonium salts such as:

diphenyloxonium tetrakis(pentafluorophenyl) borate,
 di(o-tolyl)oxonium tetrakis(pentafluorophenyl) borate, and
 di(octadecyl)oxonium tetrakis(pentafluorophenyl) borate;
 di-substituted sulfonium salts such as:

20 di(o-tolyl)sulfonium tetrakis(pentafluorophenyl) borate, and
 methylcotadecylsulfonium tetrakis(pentafluorophenyl) borate.

Preferred (L*-H)⁺ cations are methyldioctadecylammonium cations,
 dimethyloctadecylammonium cations, and ammonium cations derived from mixtures of trialkyl
 amines containing one or 2 C₁₄₋₁₈ alkyl groups.

25 Another suitable ion forming, activating cocatalyst comprises a salt of a cationic oxidizing
 agent and a noncoordinating, compatible anion represented by the formula:



wherein:

Ox^{h+} is a cationic oxidizing agent having a charge of h+;

30 h is an integer from 1 to 3; and

A^{g-} and g are as previously defined.

Examples of cationic oxidizing agents include: ferrocenium, hydrocarbyl-substituted
 ferrocenium, Ag⁺ or Pb⁺². Preferred embodiments of A^{g-} are those anions previously defined with
 respect to the Bronsted acid containing activating cocatalysts, especially
 35 tetrakis(pentafluorophenyl)borate.

Another suitable ion forming, activating cocatalyst comprises a compound which is a salt of a carbenium ion and a noncoordinating, compatible anion represented by the formula:



wherein:

5 $[C]^+$ is a C_{1-20} carbenium ion; and

A^- is a noncoordinating, compatible anion having a charge of -1. A preferred carbenium ion is the trityl cation, that is triphenylmethylum.

A further suitable ion forming, activating cocatalyst comprises a compound which is a salt of a silylium ion and a noncoordinating, compatible anion represented by the formula:



wherein:

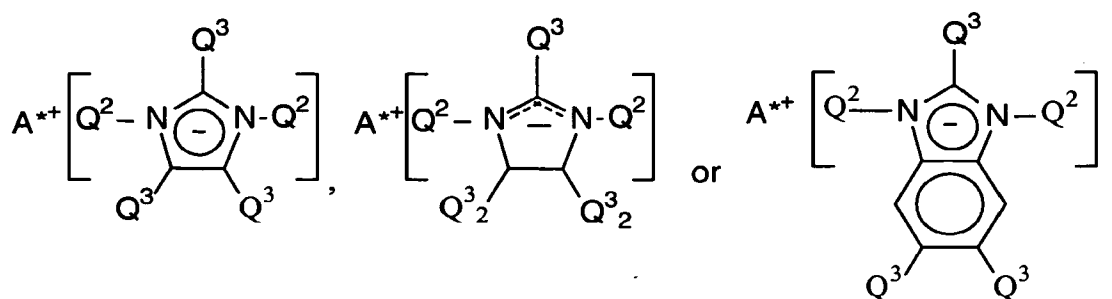
Q^1 is C_{1-10} hydrocarbyl, and A^- is as previously defined.

Preferred silylium salt activating cocatalysts are trimethylsilylium tetrakis(pentafluorophenyl)borate, triethylsilylium tetrakis(pentafluorophenyl)borate and ether
15 substituted adducts thereof. Silylium salts have been previously generically disclosed in J. Chem Soc. Chem. Comm., 1993, 383-384, as well as Lambert, J. B., et al., Organometallics, 1994, 13, 2430-2443. The use of the above silylium salts as activating cocatalysts for addition polymerization catalysts is disclosed in US-A-5,625,087.

Certain complexes of alcohols, mercaptans, silanols, and oximes with
20 tris(pentafluorophenyl)borane are also effective catalyst activators and may be used according to the present invention. Such cocatalysts are disclosed in US-A-5,296,433.

Suitable activating cocatalysts for use herein also include polymeric or oligomeric alumoxanes, especially methylalumoxane (MAO), triisobutyl aluminum modified methylalumoxane (MMAO), or isobutylalumoxane; Lewis acid modified alumoxanes, especially perhalogenated
25 tri(hydrocarbyl)aluminum- or perhalogenated tri(hydrocarbyl)boron modified alumoxanes, having from 1 to 10 carbons in each hydrocarbyl or halogenated hydrocarbyl group, and most especially tris(pentafluorophenyl)borane modified alumoxanes. Such cocatalysts are previously disclosed in US Patents 6,214,760, 6,160,146, 6,140,521, and 6,696,379.

A class of cocatalysts comprising non-coordinating anions generically referred to as
30 expanded anions, further disclosed in US Patent 6,395,671, may be suitably employed to activate the metal complexes of the present invention for olefin polymerization. Generally, these cocatalysts (illustrated by those having imidazolide, substituted imidazolide, imidazolinide, substituted imidazolinide, benzimidazolide, or substituted benzimidazolide anions) may be depicted as follows:



wherein:

A^{**+} is a cation, especially a proton containing cation, and preferably is a trihydrocarbyl ammonium cation containing one or two C_{10-40} alkyl groups, especially a methyl

5 (C₁₄₋₂₀ alkyl)ammonium cation,

Q^3 , independently each occurrence, is hydrogen or a halo, hydrocarbyl, halocarbyl, halohydrocarbyl, silylhydrocarbyl, or silyl, (including mono-, di- and tri(hydrocarbyl)silyl) group of up to 30 atoms not counting hydrogen, preferably C_{1-20} alkyl, and

Q^2 is tris(pentafluorophenyl)borane or tris(pentafluorophenyl)alumane).

10 Examples of these catalyst activators include trihydrocarbylammonium- salts, especially, methyl(C₁₄₋₂₀ alkyl)ammonium- salts of:

bis(tris(pentafluorophenyl)borane)imidazolidide,

bis(tris(pentafluorophenyl)borane)-2-undecylimidazolidide,

bis(tris(pentafluorophenyl)borane)-2-heptadecylimidazolidide,

15 bis(tris(pentafluorophenyl)borane)-4,5-bis(undecyl)imidazolidide, bis(tris(pentafluorophenyl)borane)-4,5-bis(heptadecyl)imidazolidide, bis(tris(pentafluorophenyl)borane)imidazolinide,

bis(tris(pentafluorophenyl)borane)-2-undecylimidazolinide,

bis(tris(pentafluorophenyl)borane)-2-heptadecylimidazolinide, bis(tris(pentafluorophenyl)borane)-4,5-bis(undecyl)imidazolinide, bis(tris(pentafluorophenyl)borane)-4,5-

20 bis(heptadecyl)imidazolinide, bis(tris(pentafluorophenyl)borane)-5,6-dimethylbenzimidazolidide, bis(tris(pentafluorophenyl)borane)-5,6-bis(undecyl)benzimidazolidide,

bis(tris(pentafluorophenyl)alumane)imidazolidide,

bis(tris(pentafluorophenyl)alumane)-2-undecylimidazolidide,

bis(tris(pentafluorophenyl)alumane)-2-heptadecylimidazolidide, bis(tris(pentafluorophenyl)alumane)-

25 4,5-bis(undecyl)imidazolidide, bis(tris(pentafluorophenyl)alumane)-4,5-bis(heptadecyl)imidazolidide, bis(tris(pentafluorophenyl)alumane)imidazolinide,

bis(tris(pentafluorophenyl)alumane)-2-undecylimidazolinide,

bis(tris(pentafluorophenyl)alumane)-2-heptadecylimidazolinide,

bis(tris(pentafluorophenyl)alumane)-4,5-bis(undecyl)imidazolinide,

30 bis(tris(pentafluorophenyl)alumane)-4,5-bis(heptadecyl)imidazolinide,

bis(tris(pentafluorophenyl)alumane)-5,6-dimethylbenzimidazolidine, and bis(tris(pentafluorophenyl)alumane)-5,6-bis(undecyl)benzimidazolidine.

Other activators include those described in PCT publication WO 98/07515 such as tris (2, 2', 2''-nonafluorobiphenyl) fluoroaluminate. Combinations of activators are also contemplated by the invention, for example, alumoxanes and ionizing activators in combinations, see for example, EP-A-0 573120, PCT publications WO 94/07928 and WO 95/14044 and US Patents 5,153,157 and 5,453,410. WO 98/09996 describes activating catalyst compounds with perchlorates, periodates and iodates, including their hydrates. WO 99/18135 describes the use of organoboroaluminum activators. WO 03/10171 discloses catalyst activators that are adducts of Bronsted acids with Lewis acids. Other activators or methods for activating a catalyst compound are described in for example, US Patents 5,849,852, 5,859, 653, 5,869,723, EP-A-615981, and PCT publication WO 98/32775. All of the foregoing catalyst activators as well as any other known activator for transition metal complex catalysts may be employed alone or in combination according to the present invention.

The molar ratio of catalyst/cocatalyst employed preferably ranges from 1:10,000 to 100:1, more preferably from 1:5000 to 10:1, most preferably from 1:1000 to 1:1. Alumoxane, when used by itself as an activating cocatalyst, is employed in large quantity, generally at least 100 times the quantity of metal complex on a molar basis. Tris(pentafluorophenyl)-borane, when used as an activating cocatalyst is employed in a molar ratio to the metal complex of from 0.5:1 to 10:1, more preferably from 1:1 to 6:1 most preferably from 1:1 to 5:1. The remaining activating cocatalysts are generally employed in approximately equimolar quantity with the metal complex.

During the polymerization, the mixture of monomers is contacted with the activated catalyst composition according to any suitable polymerization conditions. The process is characterized by use of elevated temperatures and pressures. Hydrogen may be employed as a chain transfer agent for molecular weight control according to known techniques if desired. As in other similar polymerizations, it is highly desirable that the monomers and solvents employed be of sufficiently high purity that catalyst deactivation does not occur. Any suitable technique for monomer purification such as devolatilization at reduced pressure, contacting with molecular sieves or high surface area alumina, or a combination of the foregoing processes may be employed.

Supports may be employed in the present invention, especially in slurry or gas-phase polymerizations. Suitable supports include solid, particulated, high surface area, metal oxides, metalloid oxides, or mixtures thereof (interchangeably referred to herein as an inorganic oxide). Examples include: talc, silica, alumina, magnesia, titania, zirconia, Sn_2O_3 , aluminosilicates, borosilicates, clays, and mixtures thereof. Suitable supports preferably have a surface area as determined by nitrogen porosimetry using the B.E.T. method from 10 to 1000 m^2/g , and preferably

from 100 to 600 m²/g. The average particle size typically is from 0.1 to 500 μm, preferably from 1 to 200 μm, more preferably 10 to 100 μm.

In one embodiment of the invention the present catalyst composition and optional support may be spray dried or otherwise recovered in solid, particulated form to provide a composition that is readily transported and handled. Suitable methods for spray drying a liquid containing slurry are well known in the art and useful for use herein. Preferred techniques for spray drying catalyst compositions for use herein are described in US-A's-5,648,310 and 5,672,669.

The polymerization is desirably carried out as a continuous polymerization, preferably a continuous, solution polymerization, in which catalyst components, monomers, and optionally solvent, adjuvants, scavengers, and polymerization aids are continuously supplied to the reaction zone and polymer product continuously removed therefrom. Within the scope of the terms "continuous" and "continuously" as used in this context are those processes in which there are intermittent additions of reactants and removal of products at small regular intervals, so that, over time, the overall process is continuous.

The catalyst compositions can be advantageously employed in a high pressure, solution, slurry, or gas phase polymerization process. For a solution polymerization process it is desirable to employ homogeneous dispersions of the catalyst components in liquid diluent in which the polymer is soluble under the polymerization conditions employed. One such process utilizing an extremely fine silica or similar dispersing agent to produce such a homogeneous catalyst dispersion where either the metal complex or the cocatalyst is only poorly soluble is disclosed in US-A-5,783,512. A high pressure process is usually carried out at temperatures from 100°C to 400°C and at pressures above 500 bar (50 MPa). A slurry process typically uses an inert hydrocarbon diluent and temperatures of from 0°C up to a temperature just below the temperature at which the resulting polymer becomes substantially soluble in the inert polymerization medium. Preferred temperatures in a slurry polymerization are from 30°C, preferably from 60°C up to 115°C, preferably up to 100°C. Pressures typically range from atmospheric (100 kPa) to 500 psi (3.4 MPa).

Preferably for use in gas phase polymerization processes, the support material and resulting catalyst has a median particle diameter from 20 to 200 μm, more preferably from 30 μm to 150 μm, and most preferably from 50 μm to 100 μm. Preferably for use in slurry polymerization processes, the support has a median particle diameter from 1 μm to 200 μm, more preferably from 5 μm to 100 μm, and most preferably from 10 μm to 80 μm.

The supported catalyst composition of the present invention can also be employed to advantage in a gas phase polymerization process. Such processes are used commercially on a large scale for the manufacture of polypropylene, ethylene/α-olefin copolymers, and other olefin polymers. The gas phase process employed can be, for example, of the type which employs a

mechanically stirred bed or a gas fluidized bed as the polymerization reaction zone. Preferred is the process wherein the polymerization reaction is carried out in a vertical cylindrical polymerization reactor containing a fluidized bed of polymer particles supported or suspended above a perforated plate or fluidization grid, by a flow of fluidization gas.

5 The gas employed to fluidize the bed comprises the monomer or monomers to be polymerized, and also serves as a heat exchange medium to remove the heat of reaction from the bed. The hot gases emerge from the top of the reactor, normally via a tranquilization zone, also known as a velocity reduction zone, having a wider diameter than the fluidized bed and wherein fine particles entrained in the gas stream have an opportunity to gravitate back into the bed. It can
10 also be advantageous to use a cyclone to remove ultra-fine particles from the hot gas stream. The gas is then normally recycled to the bed by means of a blower or compressor and one or more heat exchangers to strip the gas of the heat of polymerization.

A preferred method of cooling of the bed, in addition to the cooling provided by the cooled recycle gas, is to feed a volatile liquid to the bed to provide an evaporative cooling effect, often
15 referred to as operation in the condensing mode. The volatile liquid employed in this case can be, for example, a volatile inert liquid, for example, a saturated hydrocarbon having 3 to 8, preferably 4 to 6, carbon atoms. In the case that the monomer or comonomer itself is a volatile liquid, or can be condensed to provide such a liquid, this can suitably be fed to the bed to provide an evaporative cooling effect. The volatile liquid evaporates in the hot fluidized bed to form gas which mixes with
20 the fluidizing gas. If the volatile liquid is a monomer or comonomer, it will undergo some polymerization in the bed. The evaporated liquid then emerges from the reactor as part of the hot recycle gas, and enters the compression/heat exchange part of the recycle loop. The recycle gas is cooled in the heat exchanger and, if the temperature to which the gas is cooled is below the dew point, liquid will precipitate from the gas. This liquid is desirably recycled continuously to the
25 fluidized bed. It is possible to recycle the precipitated liquid to the bed as liquid droplets carried in the recycle gas stream. This type of process is described, for example in EP-89691; U.S. 4,543,399; WO-94/25495 and U.S. 5,352,749. A particularly preferred method of recycling the liquid to the bed is to separate the liquid from the recycle gas stream and to reinject this liquid directly into the bed, preferably using a method which generates fine droplets of the liquid within the bed. This type
30 of process is described in WO-94/28032.

The polymerization reaction occurring in the gas fluidized bed is catalyzed by the continuous or semi-continuous addition of catalyst composition according to the invention. The catalyst composition may be subjected to a prepolymerization step, for example, by polymerizing a small quantity of olefin monomer in a liquid inert diluent, to provide a catalyst composite
35 comprising supported catalyst particles embedded in olefin polymer particles as well.

The polymer is produced directly in the fluidized bed by polymerization of the monomer or mixture of monomers on the fluidized particles of catalyst composition, supported catalyst composition or prepolymerized catalyst composition within the bed. Start-up of the polymerization reaction is achieved using a bed of preformed polymer particles, which are preferably similar to the desired polymer, and conditioning the bed by drying with inert gas or nitrogen prior to introducing the catalyst composition, the monomers and any other gases which it is desired to have in the recycle gas stream, such as a diluent gas, hydrogen chain transfer agent, or an inert condensable gas when operating in gas phase condensing mode. The produced polymer is discharged continuously or semi-continuously from the fluidized bed as desired.

The gas phase processes most suitable for the practice of this invention are continuous processes which provide for the continuous supply of reactants to the reaction zone of the reactor and the removal of products from the reaction zone of the reactor, thereby providing a steady-state environment on the macro scale in the reaction zone of the reactor. Products are readily recovered by exposure to reduced pressure and optionally elevated temperatures (devolatilization) according to known techniques. Typically, the fluidized bed of the gas phase process is operated at temperatures greater than 50°C, preferably from 60°C to 110°C, more preferably from 70°C to 110°C.

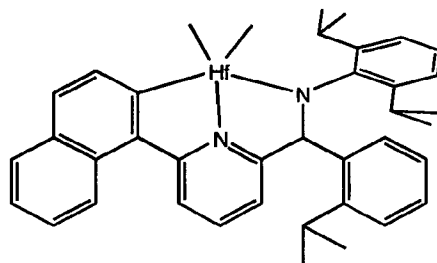
Suitable gas phase processes which are adaptable for use in the process of this invention are disclosed in US Patents: 4,588,790; 4,543,399; 5,352,749; 5,436,304; 5,405,922; 5,462,999; 5,461,123; 5,453,471; 5,032,562; 5,028,670; 5,473,028; 5,106,804; 5,556,238; 5,541,270; 5,608,019; and 5,616,661.

The skilled artisan will appreciate that the invention disclosed herein may be practiced in the absence of any component which has not been specifically disclosed.

Examples

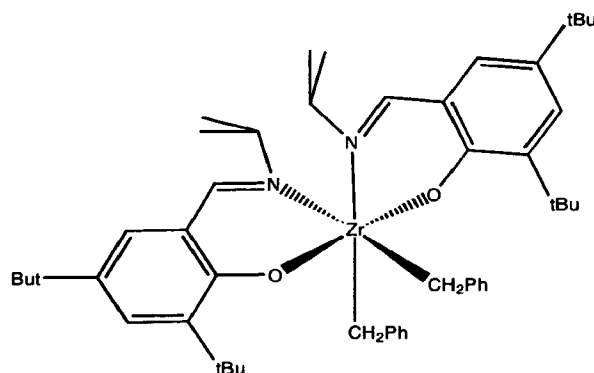
The following examples are provided as further illustration of the invention and are not to be construed as limiting. Unless stated to the contrary all parts and percentages are expressed on a weight basis. The term "overnight", if used, refers to a time of approximately 16-18 hours, the term "room temperature", refers to a temperature of 20-25 °C, and the term "mixed alkanes" refers to a commercially obtained mixture of C₆₋₉ aliphatic hydrocarbons available under the trade designation Isopar E[®], from Exxon Mobil Chemicals Inc. In the event the name of a compound herein does not conform to the structural representation thereof, the structural representation shall control. The synthesis of all metal complexes and the preparation of all screening experiments were carried out in a dry nitrogen atmosphere using dry box techniques. All solvents used were HPLC grade and were dried before their use.

MMAO refers to modified methylalumoxane, a triisobutylaluminum modified methylalumoxane available commercially from Akzo-Noble Corporation.



Cat. (A)

Catalyst (A) is [N-(2,6-di(1-methylethyl)phenyl)amido](2-isopropylphenyl)(α -naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dimethyl, prepared according to the teachings of WO 03/40195,
 5 2003US0204017, Published 10/30/2003, USSN 10/429,024, and PCT application 03/25228, filed 8/13/2003;



Cat. (B)

Catalyst (B) is (bis-(1-methylethyl)(2-oxoyl-3,5-di(t-butyl)phenyl)immino)zirconium dibenzyl.

The cocatalyst for all polymerizations is a mixture of methyldi(C₁₄₋₁₈alkyl)ammonium salts
 20 of tetrakis(pentafluorophenyl)borate, the ammonium cation of which is derived from tallowamine.

The shuttling agents employed are diethylzinc (DEZ) or triethylaluminum (TEA).

General Polymerization Conditions

Ethylene polymerizations are conducted at 130 °C and 200 psi (1.4 MPa) using 1.2
 25 equivalents of cocatalyst based on total catalyst used (1.1 equivalents when MMAO is present). A series of polymerizations are conducted in a parallel pressure reactor (PPR) comprised of 48 individual reactor cells in a 6 x 8 array that are fitted with a pre-weighed glass tube. The working

volume in each reactor cell is 6000 μL . Each cell is temperature and pressure controlled with stirring provided by individual stirring paddles. The monomer gas and quench gas are plumbed directly into the PPR unit and controlled by automatic valves. Liquid reagents are robotically added to each reactor cell by syringes and the reservoir solvent is mixed alkanes. The order of addition is solvent, monomer gas, comonomer, cocatalyst or cocatalyst/MMAO mixture, shuttling agent, and catalyst or catalyst mixture. When a mixture of cocatalyst and MMAO or a mixture of two catalysts is used, the reagents are premixed in a small vial immediately prior to addition to the reactor. When a reagent is omitted in an experiment, the above order of addition is otherwise maintained. After quenching with CO, the reactors are cooled and the glass tubes are unloaded. The tubes are transferred to a centrifuge/vacuum drying unit, and dried for 12 hours at 60 °C. The tubes containing dried polymer are weighed and the difference between this weight and the tare weight gives the net yield of polymer. Results are contained in Table 1.

Table 1

Ex.	Cat. (A) (μmol)	Cat (B) (μmol)	MMAO (μmol)	shuttling agent (μmol)	Yield (g)	Mn	Mw/Mn	hexyls ¹
A*	0.06	-	0.3	-	0.1363	300502	3.32	
B*	-	0.1	0.5	-	0.1581	36957	1.22	2.5
C*	0.06	0.1	0.8	-	0.2038	45526	5.30 ²	5.5
1	0.06	0.1		DEZ (8.0)	0.1974	28715	1.19	4.8
2	0.06	0.1		DEZ (80.0)	0.1468	2161	1.12	14.4
3	0.06	0.1		TEA (8.0)	0.208	22675	1.71	4.6
4	0.06	0.1		TEA (80.0)	0.1879	3338	1.54	9.4

* Comparative, not an example of the invention

¹ C₆ or higher chain content per 1000 carbons

² Bimodal molecular weight distribution

It may be seen the polymers produced according to the invention have a relatively narrow polydispersity (Mw/Mn) and larger content of trimer or larger blocks than polymers prepared in the absence of the shuttling agent.

Example 5 - Ethylene/1-Octene Block Copolymer

A 6-mL reaction vessel containing a glass vial insert is charged with mixed hexanes (5.383 mL), and then pressurized to 200 psi (1.4 MPa) with ethylene. Octene (157 μL), cocatalyst (1.2 mM in toluene, 0.16 mL, 192 nmol) and DEZ (80.0 mM in toluene, 0.10 mL, 8 μmol) are sequentially added via syringe. A mixture of catalyst (A) (0.60 mM in toluene, 0.10 mL, 60 nmol) and catalyst (B) (1.0 mM in toluene, 0.10 mL, 100 nmol) are added via syringe. After 60 seconds, the reaction is quenched by addition of CO. The glass insert is removed and volatile components removed under vacuum. Polymer yield = 0.197 g. Mw = 34,000; Mn = 29,000; PDI = 1.19.

Example 6 - Ethylene/1-Octene Block Copolymer

A 6-mL reaction vessel containing a glass vial insert is charged with mixed alkanes (4.483 mL), and then pressurized to 200 psi (1.4 MPa) with ethylene. Octene (157 μ L), cocatalyst (1.2 mM in toluene, 0.16 mL, 192 nmol) and DEZ (80.0 mM in toluene, 1.00 mL, 80 μ mol) are sequentially added via syringe. A mixture of catalyst (A) (0.60 mM in toluene, 0.10 mL, 60 nmol) and catalyst (B) (1.0 mM in toluene, 0.10 mL, 100 nmol) is added via syringe. After 67 seconds, the reaction is quenched by addition of CO. The glass insert is removed and volatile components removed under vacuum. Polymer yield = 0.147 g. Mw = 2,400; Mn = 2,200; PDI = 1.12.

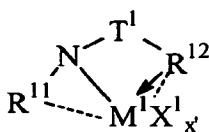
Comparative D - Ethylene/1-Octene Copolymer Mixture

A 6-mL reaction vessel containing a glass vial insert is charged with mixed alkanes (5.323 mL), and then pressurized to 200 psi (1.4 MPa) with ethylene. Octene (157 μ L), and then a mixture of cocatalyst (1.2 mM in toluene, 0.16 mL, 192 nmol) and MMAO (5.0 mM in toluene, 0.16 mL, 800 nmol) is added via syringe. A mixture of catalyst (A) (0.60 mM in toluene, 0.10 mL, 60 nmol) and catalyst (B) (1.0 mM in toluene, 0.10 mL, 100 nmol) was added via syringe. After 87 seconds, the reaction is quenched by addition of CO. The glass insert is removed and volatile components removed under vacuum. Polymer yield = 0.204 g. Mw = 241,000; Mn = 46,000; PDI = 5.30 with a bimodal distribution, indicating formation of two separate polymers and little or no interaction between different catalyst centers.

Examples 5 and 6 demonstrate the synthesis of linear block copolymers by the present invention as evidenced by the formation of a very narrow MWD monomodal copolymer when DEZ is present and a bimodal, broad molecular weight distribution product (a mixture of separately produced polymers) in the absence of DEZ. Due to the fact that Catalyst (A) is known to incorporate more octene than Catalyst (B), the different blocks or regions of the resulting copolymers of Examples 5 and 6 are distinguishable based on branching or density.

CLAIMS:

1. A catalyst composition for use in polymerization of ethylene and at least one copolymerizable comonomer, to form a high molecular weight, segmented, ethylene copolymer, said copolymer containing therein two or more segments differing in comonomer content or density,
5 the catalyst composition comprising the admixture or reaction product resulting from combining:
(A) a first metal complex olefin polymerization catalyst having a high comonomer incorporation index,
(B) a second metal complex olefin polymerization catalyst having a comonomer incorporation index less than 95 percent of the comonomer incorporation index of catalyst (A), and
10 (C) a chain shuttling agent.
2. A catalyst composition according to claim 1 wherein catalyst (B) has a comonomer incorporation index less than 10 percent of catalyst (A).
- 15 3. A catalyst composition according to claim 1 wherein the shuttling agent has an activity ratio R_{A-B}/R_{B-A} of from 0.1 and 100, wherein R_{A-B} is the rate of polymeryl exchange from catalyst A active site to catalyst B active site via the shuttling agent, and R_{B-A} is the rate of exchange from catalyst B active site to catalyst A active site via the shuttling agent.
- 20 4. A catalyst composition according to claim 1 wherein less than 90 percent of shuttle-polymeryl products are terminated prior to attaining 3 distinguishable polymer segments or blocks.
5. A catalyst composition according to claim 1 wherein the shuttling agent is a trihydrocarbyl aluminum- or dihydrocarbyl zinc- compound containing from 1 to 12 carbons in each
25 hydrocarbyl group.
6. A catalyst composition according to claim 5 wherein the shuttling agent is triethylaluminum or diethylzinc.
- 30 7. A catalyst composition according to claim 1 wherein catalyst (A) is a complex comprising a transition metal selected from Groups 4-8 of the Periodic Table of the Elements and one or more delocalized, π -bonded ligands or polyvalent Lewis base ligands.
8. A catalyst composition according to claim 7 wherein catalyst (A) corresponds to the
35 formula:



wherein:

R^{11} is selected from alkyl, cycloalkyl, heteroalkyl, cycloheteroalkyl, aryl, and inertly substituted derivatives thereof containing from 1 to 30 atoms not counting hydrogen;

5 T^1 is a divalent bridging group of from 1 to 20 atoms other than hydrogen;

R^{12} is a C_{6-20} heteroaryl group containing Lewis base functionality;

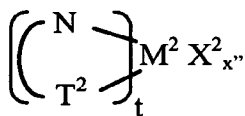
and in the metal complex, M^1 is a Group 4 metal;

X^1 is an anionic, neutral or dianionic ligand group;

x' is a number from 0 to 5 indicating the number of such X^1 groups; and

10 bonds, optional bonds and electron donative interactions are represented by lines, dotted lines and arrows respectively.

9. A catalyst composition according to claim 8 wherein catalyst (B) corresponds to the formula:



15 wherein

M^2 is a metal of Groups 4-10 of the Periodic Table of the elements;

T^2 is a nitrogen, oxygen or phosphorus containing group;

X^2 is halo, hydrocarbyl, or hydrocarbyloxy;

20 t is one or two;

x'' is a number selected to provide charge balance;

and T^2 and N are linked by a bridging ligand.

ABSTRACT

A catalyst composition for use in polymerization of ethylene and at least one copolymerizable comonomer, to form a high molecular weight, segmented, ethylene copolymer, said copolymer containing therein two or more segments differing in comonomer content or density, a polymerization process using the same and the resulting polymers, the catalyst composition comprising the admixture or reaction product resulting from combining:

(A) a first metal complex olefin polymerization catalyst having a high comonomer incorporation index,

(B) a second metal complex olefin polymerization catalyst having a comonomer incorporation index less than 95 percent of the comonomer incorporation index of catalyst (A), and

(C) a chain shuttling agent.